

**IMPACT OF FERTILIZER PLACEMENT ON PHOSPHORUS IN CROP,
SOIL, AND RUN-OFF WATER IN A BROWN CHERNOZEM IN SOUTH-
CENTRAL SASKATCHEWAN**

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Saskatoon

By

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ABSTRACT

Fertilizer phosphorus (P) application rate and method are anticipated to have important influences on crop utilization and concentration and distribution of residual P in soil. This, in turn, can influence the amount of P removed in run-off water. The objective of this thesis work was to assess the influence of fertilizer P application method and rate on soybean (*Glycine max* (L.)) emergence, yield, and P uptake. Additionally, the forms and distribution of residual soil P following a season of crop growth, and the off-site export of applied P in simulated snowmelt run-off water was assessed. In a controlled environment study, soybean could tolerate up to 20 kg P₂O₅ ha⁻¹ placed in the seed-row without significant reduction in emergence. Soybean was grown in a field study in 2014 in south-central Saskatchewan. Two sites were utilized within the same wheat stubble field (Downslope and Upslope) where fertilizer P was soil applied in the spring (seed-placed, deep band, and broadcast and incorporated) at 20 kg P₂O₅ ha⁻¹ and broadcast at three rates (20, 40, and 80 kg P₂O₅ ha⁻¹), along with a control treatment receiving no fertilizer P. At the Downslope position, in-soil application of fertilizer P resulted in a greater soybean yield and P uptake than broadcast application. After harvest, higher labile P concentrations were found in the zone of fertilizer P placement in the soil. Elevated concentrations of water soluble P were noted near the soil surface with broadcast P application compared to in-soil placement methods, attributed to immobility of P and lower plant utilization. A simulated snowmelt run-off event was conducted on intact soil slabs removed from the Upslope position treatments. Fertilizer P application method had a significant influence on P export with the greatest export occurring with broadcast application. Phosphorus XANES spectroscopy provided further evidence that, qualitatively, fertilizer P application method influenced speciation of fertilizer P reaction products in calcareous soil common to the Canadian prairies. Overall, it is concluded that in-soil placement of P fertilizer is a beneficial management practice in a prairie soil to maximize agronomic benefit while minimizing potential transport of fertilizer P off the field in snowmelt run-off water.

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DEDICATION

As with all things in my life, this work is first and foremost dedicated to my Lord and Savior Jesus Christ, to whom I owe everything.

‘Tis mystery all! Th’Immortal dies!
Who can explore His strange design?
In vain the firstborn seraph tries
To sound the depths of love divine!
‘Tis mercy all! let earth adore,
Let angel minds inquire no more.
Amazing love! how can it be
That Thou, my God, should die for me!
-Charles Wesley

I would also like to dedicate this work to my loving wife Meagan, without whom this would not be possible. Finally, special thanks to both of my sets of parents David and Irene and Don and Donna. Thanks for all your support!

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collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control. 77

Fig. 4.19. Mean exchangeable P ($\mu\text{g P cm}^{-2}$) as a function of fertilizer P application method measured at the soil-runoff water interface during a simulated runoff experiment. Error bars represent the standard error of the four replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); DB: Deep band ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B/I: Broadcast with incorporation ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(20): Broadcast ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(40): Broadcast ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and B(80): Broadcast ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control. 78

Fig. 4.20. Mean total P concentration (mg kg^{-1}) of the particulate fraction collected following vacuum filtration of runoff water samples from a simulated runoff experiment as a function of fertilizer P application method. Error bars represent the standard error of the four replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); DB: Deep band ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B/I: Broadcast with incorporation ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(20): Broadcast ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(40): Broadcast ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and B(80): Broadcast ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control. 79

Fig. 4.21. TDP (Total Dissolved Phosphorus) export (kg TDP ha^{-1}) from water leaching soybean residue after a simulated freeze-thaw cycle at the Downslope position. Error bars represent the standard error of the four field replicates of each treatment. A description the of the treatments is as follows: C: Control; (no P) SP: Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); DB: Deep band ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B/I: Broadcast with incorporation ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(20): Broadcast ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(40): Broadcast ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and B(80): Broadcast ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control. 80

Fig. 4.22. TDP (Total Dissolved Phosphorus) export (kg TDP ha^{-1}) from soybean residue after a simulated freeze-thaw cycle at the Upslope position. Error bars represent the standard error of the four field replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); DB: Deep band ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B/I: Broadcast with incorporation ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(20): Broadcast ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(40): Broadcast ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and B(80): Broadcast ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control. 81

Fig. A1. Soil test report from soil cores collected from the Downslope field site location in Spring 2014. A composite subsample was collected from eight individual soil cores collected in April from the marked out control plots before any treatments or field operations were conducted. 112

Fig. A2. Soil test report from soil cores collected from the Upslope field site location in Spring 2014. A composite subsample was collected from eight individual soil cores collected in April from the marked out control plots before any treatments or field operations were conducted. . 113

LIST OF ABBREVIATIONS

Aluminum	Al
Atomic Absorption-Flame Emission	AA-FE
Best Management Practice	BMP
Calcium	Ca
Canadian Light Source	CLS
Copper	Cu
Dissolved Reactive Phosphorus	DRP
Electron Volts	eV
Ethylenediaminetetraacetic acid	EDTA
Hydrochloric Acid	HCl
Inorganic Phosphorus	P _i
Iron	Fe
Linear Combination Fitting	LCF
Magnesium	Mg
Manganese	Mn
Modified Kelowna	KM
Mono Ammonium Phosphate	MAP
Nitrate	NO ₃ ⁻
Nitrogen	N
Nuclear Magnetic Resonance	NMR
Organic Phosphorus	P _o
Phosphate	PO ₄ ³⁻
Phosphorus	P
Potassium	K
Principal Component Analysis	PCA
Revolutions Per Minute	RPM
Sodium Hydroxide	NaOH
Soft X-ray Microcharacterization Beamline	SXRMB
Soil Test Phosphorus	STP
Sulfuric Acid	H ₂ SO ₄ ⁻
Total Dissolved Nitrogen	TDN
Total Dissolved Phosphorus	TDP
Total Organic Carbon	TOC
X-ray Absorption Near Edge Structure	XANES
Zinc	Zn

1. INTRODUCTION

1.1 Phosphorus Status of Agricultural Soils

Soil test phosphorus (P) levels measured in agricultural soils on the Canadian prairies are characterized by an apparent dichotomy, where certain soils are excessively enriched from manure and fertilizer applications and can contribute to elevated P in run-off water, while others are classified as deficient for crop production and require P fertilization. This distinction may be due in large part to agricultural nutrient management practices, where application rate and method may have a profound influence on the concentration and distribution of P in soil (Havlin et al., 2014). For example, scrutiny has been placed on agricultural soils that have had excessive rates or improper applications made as a source of dissolved reactive phosphorus (DRP) entering surface water bodies on the Canadian prairies. As such, there is increased interest in understanding how management practices such as fertilizer or manure addition may influence the amount of soluble P entering surface water through runoff (Kumaragamage et al., 2011). This seems justified, as it has been estimated that present day agriculture is responsible for 15% of the P load that enters Lake Winnipeg, a water body with severely impacted water quality (Lake Winnipeg Stewardship Board, 2006). The negative influence that P additions have on water quality are well documented, as P is one of the major nutrients shown to contribute to eutrophication (Schindler, 2006; Carpenter, 2008). On the Canadian prairies, the spring period from April to July has been identified as the critical period for the entry of DRP from soil and crop residue into water running across frozen soil and infiltrating through the thawing surface layer of soil (Lake Winnipeg Stewardship Board, 2006).

Phosphorus fertilizer on the prairies is commonly recommended for placement in the seed-row to provide a supply of “starter” P to the roots of annual crops early on in their life cycle (Government of Saskatchewan, 2012). However, there is a limit to how much P can be safely placed in the seed-row for crops. Grant (2012) suggested that increased production of crops sensitive to seed-placed fertilizer P on the Canadian prairies, such as canola, flax and pulse crops, may lead to deficiencies in Soil Test P (STP) in certain soils, as crop removal of soil P in

harvested material exceeds P input that is currently recommended to be safely applied with the seed. As an alternative to fertilizer placement in the seed-row, growers may choose to separately band, broadcast and incorporate, or even simply broadcast fertilizer P on the surface when high rates of fertilizer P are recommended. There is a need to understand how the different approaches to fertilizer P placement may affect not only crop yield response, but also export of P in spring snowmelt water.

1.2 Identification of Soil Phosphorus Forms

Due to the complex nature of the soil matrix, the use of a combination of spectroscopic techniques, such as X-ray Adsorption Near Edge Structure (XANES) spectroscopy, ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy, and chemical separations such as sequential chemical extraction, are most effective in revealing P speciation in soil (Liu et al., 2015). Each of the aforementioned techniques has its own unique advantages and limitations, and can provide insight into an aspect of soil P speciation and thereby potential plant availability and mobility. For example, XANES spectroscopy has been suggested as an effective method for elucidating speciation of inorganic P (P_i) in soil. Advantages of this technique include its high level of elemental specificity, as well as its ability to determine the local chemical and structural environment of an element and its oxidation state (Ajiboye et al., 2008). Many researchers have used XANES spectroscopy as a fingerprinting technique. This typically involves the application of statistical methods such as Linear Combination Fitting (LCF) and Principal Component Analysis (PCA) to match the spectra collected from known standard compounds with unique spectral features to the spectrum of an unknown sample (Ajiboye et al., 2007; Ajiboye et al., 2008; Kar et al., 2012; Khatiwada et al., 2012). Additionally, ^{31}P NMR spectroscopy has been identified as a quantitative technique which has the potential to identify all P species in soil, and which has been shown to be particularly useful in identifying organic P (P_o) species (Cade-Menun, 2005a; Liu et al., 2015).

Chemical identification of labile, potentially mobile soil P fractions has mainly relied on different “soil test” extractions (Stumborg and Schoenau, 2008) while sequential chemical extractions attempt to extract various operationally defined soil P pools, and relate these pools to their relative bioavailability to a plant. A sequential procedure employing various extractants is deemed valuable in revealing P cycling as a plant will take up readily available P from the soil

solution, as well as P that is released into solution over time. As such the content of P in the different fractions is anticipated to change in both the short and longer term. The utility of these chemical extraction techniques is based on them being simple enough for routine application, and also that they can be correlated to functional parameters such as P bioavailability, mobility, reactivity, and crop response (Tiessen and Moir, 2008). Spectroscopic information provided through XANES and ^{31}P NMR may be used in tandem with the results of a sequential chemical extraction to examine relationships between P management practices, the speciation of fertilizer P reaction products in soil, and their relative plant availability and potential mobility.

Khatiwada et al. (2012) demonstrated that fertilizer application method influences the speciation of fertilizer P reaction products in an incubation study conducted in an acidic soil in the absence of crop growth. Sparks (2003) noted that many chemical reactions occurring in soil are time-dependent, and a consideration of reaction kinetics is therefore warranted. Thus it may be beneficial to assess the effect that fertilizer application method has on the speciation of fertilizer P reaction products after a season of crop growth, as uptake of P by the crop may influence the amount and type of P containing compounds formed. It would be especially beneficial to study this effect in a calcareous soil, which is typical of the Canadian prairies. An understanding of the speciation of fertilizer P reaction products will help in predicting the environmental fate of applied P following a snowmelt run-off event.

1.3 Justification of Research

Recent trends have shown increased interest among agricultural producers in the broadcast application of fertilizer to improve operational efficiency, especially to speed up the spring seeding and fertilization operation compared to placement in soil (Lyseng, 2014). Previous research has shown that broadcast fertilizer P leads to significant enrichment in soil P near the soil surface, and the lack of enrichment from banded application has been suggested as a strategy to mitigate P contamination of surface water bodies (Borges and Mallarino, 2000). Given this, quantitative information is lacking as to how in-soil placement versus surface broadcast application would affect the transport of P off-site in snowmelt water on the Canadian prairies. This research question is assessed in this thesis through a simulated snowmelt run-off experiment. Furthermore, research has shown that fertilizer placement strategy (i.e. broadcast versus deep band) has a profound influence on the speciation of fertilizer P reaction products

under reduced-tillage management systems (Khatiwada et al., 2012). However, this effect has not been quantified under soil conditions evident in the Canadian prairies. Finally, soybean (*Glycine max* (L.)) is a grain legume crop that has been gaining popularity among agricultural producers on the Canadian prairies, especially the eastern prairies, in recent years (Risula et al., 2015a). Little information exists, however, regarding its response to P fertilization practices under Canadian prairie conditions. Therefore, soybean yield and P uptake in response to fertilizer P placement was evaluated, as well as its sensitivity to different rates of fertilizer P applied in the seed-row.

1.4 Hypotheses and Objectives

In light of the above information and gaps in knowledge identified above, the following hypotheses were proposed:

- (i) In-soil placement of fertilizer P at the time of seeding in spring will increase crop uptake and recovery of P by soybean and reduce P transport in spring snowmelt compared to the surface broadcast method of fertilizer P application.
- (ii) Speciation of fertilizer P reaction products in soil will be influenced by method of fertilizer P application in calcareous soils common to the Canadian prairies.

The major objectives of this study are as follows:

- (i) Quantify the effect of method and rate of fertilizer P application on crop yield, emergence, P uptake, and use efficiency by short-season soybean, and the concentration and export of P in simulated snowmelt run-off water.
- (ii) Determine the various P forms present in the soil at the end of the growing season through application of XANES spectroscopy, as well as chemical extractions.
- (iii) Examine relationships between P fertilization practice, crop responses, residual soil P forms and the export of P in snowmelt run-off water.

1.5 Organization of Thesis

This thesis is presented as a collection of chapters which are formatted for the purpose of submission to peer reviewed journals. The first chapter introduces the topic of the thesis, while

the second chapter provides a review of relevant literature. Chapters 3 and 4 are research chapters, which each address an important research question in this thesis. Chapter 3 consists of two agronomic studies to assess the effect of fertilizer application method and rate on seedling emergence, crop yield, and P uptake. The fourth chapter covers the effect that fertilizer P application method has on influencing residual soil P distribution and the P export from the soil system in simulated snowmelt run-off. A synthesis of the findings, emphasizing relationships among the parameters assessed, along with conclusions and suggestions for future research are presented in Chapter 5. References cited throughout the text are listed in Chapter 6. Appendix A contains supplemental data and details on the statistical analysis (ANOVA tables) for parameters which were measured over the course of the study. Additionally, a series of soil test reports are provided in Appendix A to provide further baseline information on the soils at the sites described in Chapter 3.

2. LITERATURE REVIEW

2.1 The Soil Phosphorus Cycle

2.1.1 Internal phosphorus cycling

To predict the fate of P added to soil as fertilizer, it is beneficial to have an understanding of its biogeochemical cycle, focusing first on internal cycling within the local soil environment. Phosphorus that is directly available for biological assimilation and also potentially mobile is contained in the soil solution. Soil solution P exists largely as orthophosphate ions (H_2PO_4^- and HPO_4^{2-}) as well as certain soluble organic P compounds, as illustrated in Fig. 2.1 below. Importantly, the chemical speciation of the orthophosphate ion existing in a given soil environment is a function of soil pH, whereby H_2PO_4^- dominates in strongly acidic soils (pH 4 to 5.5) and HPO_4^{2-} dominates in basic soils (pH 7.2 or higher) (Brady and Weil, 2008). Losses of P from soil solution are buffered by additions from other soil P pools. For example, orthophosphate ions may be removed from solution via reaction with calcium (Ca) minerals via precipitation or adsorption under basic soil conditions, adsorbed to clay minerals, or oxides of iron (Fe) and aluminum (Al) under acidic soil conditions (Fig. 2.1 a). Phosphorus that is loosely sorbed or held in the solid phase in the form of relatively soluble precipitates is often referred to as labile inorganic P. Further, dissolution of primary and secondary P minerals of low solubility, known as nonlabile inorganic P, may occur, thereby replenishing the solution P pool (Holford, 1997; Brady and Weil, 2008) (Fig. 2.1 b). It is also important to note that both adsorption and desorption and precipitation and dissolution are time-dependent processes, and as such, a consideration of reaction kinetics is warranted to understand short-term P dynamics (Sparks, 2003). Terms to describe the rates of these reactions are K_{so} and K_{sp} , respectively.

Organic P compounds are also important in the soil P cycle, not surprising as in some soils they constitute 50% or more of the total soil P pool. Although only approximately 50% of all organic soil P compounds have been identified, a majority of the known compounds have been characterized as esters of orthophosphoric acid (H_2PO_4^-). Microbial activity results in the

release of orthophosphate ions through mineralization and immobilization processes, as well as decomposition of plant biomass, thus contributing to the solution P pool (Turner et al., 2007; Havlin et al., 2014) (Fig. 2.1 d and g).

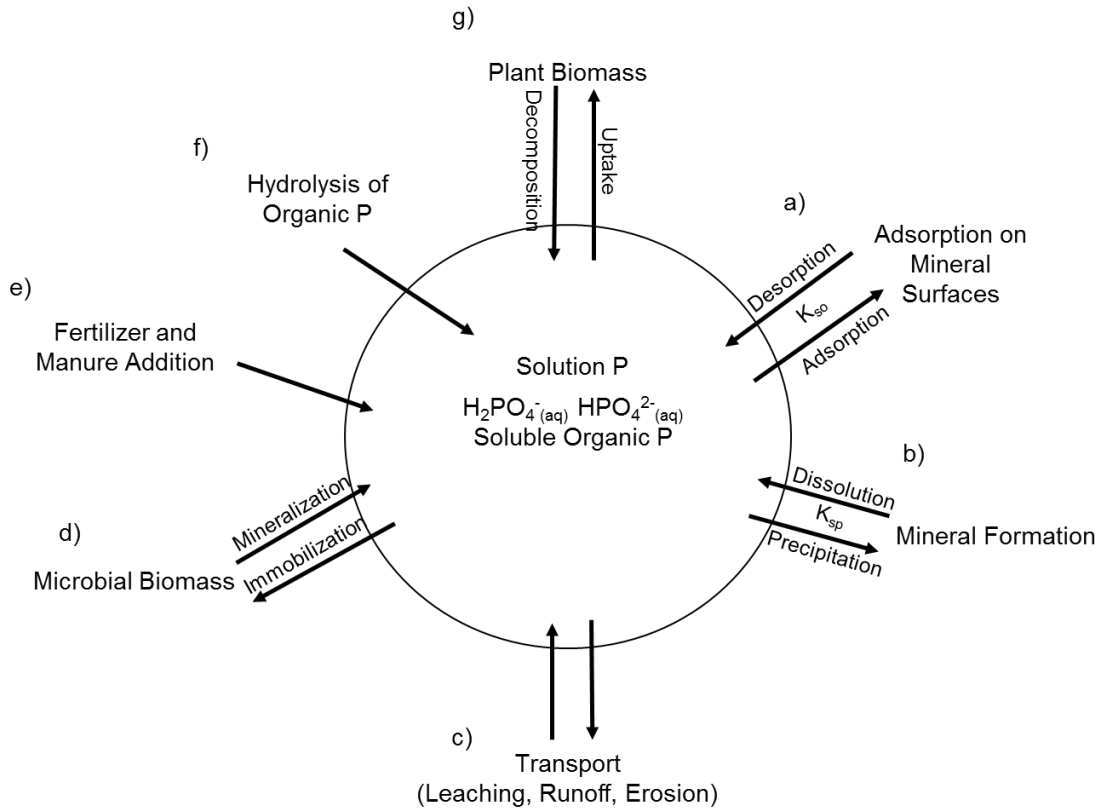


Fig. 2.1. Conceptual diagram of the P cycle in an agroecosystem.

2.1.2 Inputs

The P cycle may also be examined from a perspective of inputs to, and losses from, the soil system. Inputs of plant available P into the solution P pool may be either inorganic or organic. The phosphate (PO_4^{3-}) in inorganic fertilizers is initially water soluble but when they dissolve, reactions occur to make the phosphate less soluble and available (Condon, 2004). Added fertilizer P granules such as mono ammonium phosphate (MAP) dissolve in soil solution to release inorganic orthophosphate ions that subsequently react with clay particles or form minerals which can subsequently undergo dissolution when the soil solution is depleted of phosphate by plant uptake or leaching (Arai and Sparks, 2007). Other highly soluble, liquid P fertilizers may be added as a direct input to the solution P pool (Brady and Weil, 2008).

Low molecular weight, soluble organic P containing compounds are derived from decaying plant, animal, and microbial biomass and can enter into the soil solution (Fig. 2.1 d and g) where they may be mineralized to orthophosphate or directly used by plants (Condrón et al., 2005). Further, application of cattle manure may lead to significant additions of P to soil, especially when manure is applied annually to meet crop demand for N (Stumborg and Schoenau, 2008). Transformations of organic P can have considerable effect on the bioavailability and mobility of P in soil (Turner et al., 2007). However, these organic P compounds generally make a lesser contribution to total bioavailable P than inorganic compounds. It is important to note that the relative bioavailability of organic P compounds varies. For example, inositol hexaphosphate has the ability to form insoluble salts, binding to Fe^{3+} and Al^{3+} under acidic soil pH and Ca^{2+} under basic soil conditions, as well as its ability to participate in strong complexation reactions with proteins (Richardson, 1994). Each of these reactions causes the inositol hexaphosphate to be protected from enzymatic attack, and thus less bioavailable. On the other hand, other organic P compounds exist in soil, such as phospholipids, which, although insoluble, are readily immobilized by soil microorganisms (Havlin et al., 2014). Mineralization of organic P is dependent on microbial activity as influenced by temperature, moisture, redox, as well as the composition of the substrate, including the C:P ratio (Turner et al., 2007). The production and activity of phosphatase enzymes in the rhizosphere can also control the release of ester bonded phosphates in the soil organic matter.

2.1.3 Outputs

2.1.3.1 Biological uptake of phosphorus

Phosphorus is a plant essential macronutrient that must be taken up by soybean in sufficient quantities to maintain homeostasis and contribute to growth. So important is this element to plant nutrition that it constitutes approximately 0.2 % of a plant's dry weight, broadly partitioned into vegetative tissue and the seed. Movement of P through the bulk soil occurs mainly by diffusion at rates ranging from 10^{-12} to $10^{-15} \text{ m}^2 \text{ s}^{-1}$, which limits uptake by roots, creating a microenvironment surrounding the root that is depleted of soil P (Schachtman et al., 1998). For this reason, plant root geometry and morphology are instrumental in maximizing soil P uptake, as root systems having high surface area to volume ratios are able to explore large soil

volumes (Lynch, 1995). Research has shown that soil P_i is largely taken up in the $H_2PO_4^-$ form (Ullrich-Eberius et al., 1984) and it has been suggested that it occurs by cotransport of P_i with one or several protons (Schachtman et al., 1998). Soil microorganisms are also active in mineralization and immobilization of soil P, thereby either adding or removing plant available P from the soil P pool. Additionally, mycorrhizal fungi may form a symbiotic relationship with plants, and contribute to uptake of soil P as fungal hyphae substantially increase the soil volume that plant roots are able to explore (Smith and Read, 1997).

Once taken up by a plant, soil P_i is distributed either into vegetative tissues or the seed, each with its own favored storage mechanism. For example, at physiological maturity, about 90% of P_i in plant leaves is stored in the cell organelle known as a vacuole (Lauer et al., 1989). In seeds, however, P_i is predominantly found in the storage compound phytic acid (Bielecki, 1973). As plant growth occurs, P_i stored in vacuoles is remobilized and transferred to the seed, most notably during the R6 growth stage of soybean (Lauer et al., 1989). In total, approximately 50 % of the P_i present in seed is translocated from elsewhere in the plant (Hanway and Weber, 1971). Much of the soil P that is taken up by plants remains in the seed. For example, approximately 70% of the total P content of cereal grains is found in the seed (Rose et al., 2013) and this percentage increases for certain pulse crops (Government of Saskatchewan, 2012). As a result, appreciable quantities of P_i taken up by plants is removed from the place of origin in the form of harvested grain (Government of Saskatchewan, 2012). For soybean, Grant (2012) reported that based on a grain yield of 2695 kg ha^{-1} , $35.8 \text{ kg P ha}^{-1}$ would be removed in the form of harvested grain.

2.1.3.2 Phosphorus export in leaching water

It is important to account for P losses from a given soil system. Although P leaching from soils has been generally considered as relatively minor loss mechanism from an agronomic standpoint, P transport with water may occur as dissolved organic and inorganic P over long time periods during pedogenesis, altering P distribution in the profile (Schoenau et al., 1987). Sandy soils with low P sorption capacity may also be prone to P export by leaching, especially when loaded with P from excessive fertilizer or manure applications. Significant amounts of P were observed in tile drainage systems from Gleysols in Quebec (Simard and Beauchemin, 2002).

Downward movement of P may either occur through leaching through the soil micropores, or via preferential flow through macropores such as soil cracks, plant root channels, and bores created by earthworms. Examples of conditions that promote downward movement of P via leaching include the presence of deep, sandy horizons within the soil profile, soils of high organic matter, and under management conditions whereby either synthetic fertilizer P or animal manure is applied year after year at rates in excess of annual crop removal (Sims et al., 1998). In particular, downward movement of P in deep, sandy soils is exacerbated by frequent, heavy rainfall events. For example, P enriched soil was found at a depth of 90 cm in a soil from Florida having deep, sandy profile development and which had received 1680 to 3360 kg superphosphate fertilizer (0-45-0) $\text{ha}^{-1} \text{ year}^{-1}$ (Bryan, 1933). The potential of P leaching arising when high rates of cattle manure are applied annually as an input to the soil P pool was demonstrated by Whalen and Chang (2001). After 16 years of annual application at rates of 30, 60, and 90 Mg manure ha^{-1} on nonirrigated soils and 60, 120, and 180 Mg manure ha^{-1} on irrigated soils in Lethbridge, Canada, total P in the soil was determined to be 1.2 to 3.8 Mg P ha^{-1} and 1.9 to 5.2 Mg P ha^{-1} greater than the control treatment on the two soils, respectively to a depth of 150 cm. Further, an assessment of P input in manure and P measured in soil and crop pools was conducted, and it was demonstrated that between 7 and 15% of the applied P in irrigated soils could not be accounted for to a depth of 150 cm. It was therefore suggested that this unaccounted P may have been lost in surface runoff or leached to groundwater (Whalen and Chang, 2001).

2.1.3.3 Runoff losses

Runoff losses of P from the point of application may be subdivided into particulate and dissolved P forms, with the distinction made on the basis of separation through a 0.45- μm pore diameter membrane filter (Cade-Menun et al., 2006). Research has shown that orthophosphate dominates the dissolved P fraction. This is relevant, as orthophosphate ions are highly bioavailable to both terrestrial plants and aquatic organisms like macrophytes and algae. The composition of particulate P is more variable in nature, consisting of P adsorbed to soil particles and organic matter that has been displaced from its place of origin via erosive processes (Sharpley et al., 1994). The bioavailability of the particulate P in runoff water is also highly variable, and largely a function of land management practices occurring in the watershed with estimates of contribution of particulate P ranging from 9 to 69 % in one study (Sharpley et al.,

1992). In addition to its role in influencing the relative bioavailability of particulate P, land management practices also affects the total amount of eroded P, as soil fractions having a relatively small particle size, such as clay and colloidal organic matter, are selectively eroded. Practically, this causes the eroded material to be enriched in P compared to the source soil as the clay and colloidal organic matter is typically enriched in P relative to coarser, more dense, less mobile particulate fractions. The degree of this enrichment is substantial, as researchers have shown eroded soil to be enriched with STP, as tested by the Bray I extraction procedure, in runoff by a factor of 1.87 to 2.72 under simulated rainfall conditions (Sharpley, 1985). However, it is important to note that much of the eroded particulate P never enters a permanent surface water body, as it generally does not leave its field of origin (McIsaac et al., 1995). Instead, in Western Canada, it is reported that much of the long-distance P transport that occurs via run-off, takes place in the spring snowmelt period as dissolved orthophosphate in the snowmelt runoff water (Glozier et al., 2006; Little et al., 2007).

2.1.4 Crop residue as a source of phosphorus

One of the objectives of the work in this thesis was to assess the effect that fertilizer P application method has on influencing the concentration of orthophosphate in runoff water. As fertilizer P application strategy is anticipated to influence availability of the fertilizer P for soybean uptake, and consequently P concentration of soybean residue, P in crop residue may have important implications for the offsite transport of P in runoff water. It has been suggested that a consideration of crop residue as a source of soluble P is necessary in light of increased implementation of conservation tillage practices that maintain large amounts of P on the soil surface (Liu et al., 2013). Significant nutrient enrichment at the soil surface may also occur from nutrients that are leached from crop residue that is left on the soil surface under a conservation tillage management system (Sharpley and Smith, 1989). For example, Langdale et al. (1985) observed that the concentration of dissolved P in runoff water from soybean residue was greater under conservation tillage compared to a conventional tillage management system. Cermak et al. (2004) conducted an incubation study where soybean residue was exposed to solutions of varying concentrations of orthophosphate and with different solution / residue contact times. It was determined that leaching of P was not influenced by the P concentration of the solution, but was deemed to be affected by solution / residue contact time. Additionally, corn and winter

wheat residues were included in the incubation study, and it was determined that the amount of P leached was influenced by the P concentration of the crop residue (Cermak et al., 2004).

2.2 Phosphate Chemistry

2.2.1 Phosphate speciation

When studying the chemistry of P_i in soil, one is primarily concerned with the tetrahedral PO_4^{3-} oxyanion, and the complexes that this ligand forms with various cations in soil solution. As orthophosphate may be considered a weak Lewis Base in soil solution, it does not completely dissociate in water. Consequently, one may see how speciation changes as a function of solution pH, as illustrated in Fig. 2.2 below. Primary orthophosphate ($H_2PO_4^-$) dominates in strongly acidic soils (pH 4 to 5.5), while secondary orthophosphate (HPO_4^{2-}) dominates in basic soils (pH 7.2 to 12).

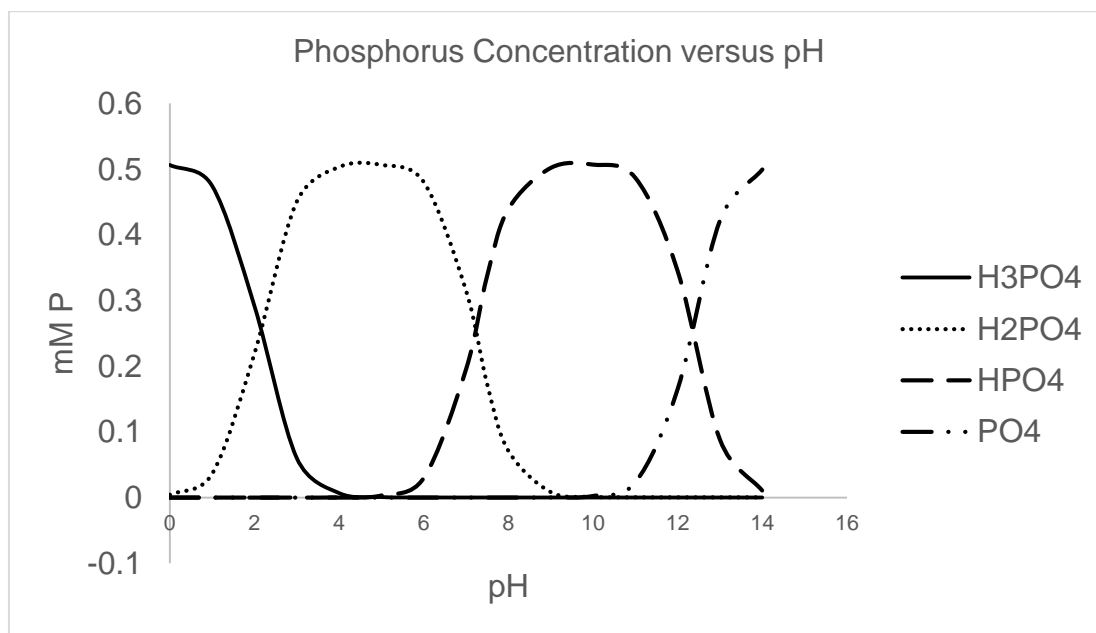


Fig. 2.2. Graph showing the pH dependency of phosphate ligand speciation in solution.

2.2.2 Phosphate complexation in soils

Pearson's Hard/Soft Acid Base Theory (Pearson, 1963) explains the complexation that phosphate undergoes with metals in the soil solution. Pearson's theory provides a means to

predict the tendency of metals and ligands to form complexes. Pearson's theory states that metals behave as acids in this situation, while ligands behave as bases. The division between hard and soft acids and hard and soft bases is based on several characteristics. For example, a hard acid is characterized by its high positive charge, small ionic radius, and absence of easily excited valence electrons, while a soft acid is known for its low positive charge, large ionic radius, and presence of easily excited valence electrons. On the other hand, a hard base is characterized by the donor atom (i.e. Lewis Base) possessing high electronegativity, low polarizability, and the unavailability of empty orbitals, while a soft base is characterized by the donor atom having low electronegativity, high polarizability, and the presence of easily accessible empty orbitals (Lemire et al., 2013). Finally, Pearson's theory states the tendency of metals to form bonds with ligands of similar type, in that a hard acid (i.e. metal) would tend to form a complex with a hard base (i.e. ligand), and vice versa (Pearson, 1963).

The PO_4^{3-} -metal complexes that tend to form in soil are expected according to Pearson's Hard/Soft Acid Base Theory, which states that metals tend to form complexes with ligands of the same type. For example, it has been observed that phosphate ions tend to form complexes with Ca^{2+} ions under basic soil conditions, while they tend to form complexes with Fe^{3+} or Al^{3+} ions under acidic soil conditions. Pearson's theory would predict the formation of these complexes, as PO_4^{3-} may be classified as a hard base, while Ca^{2+} , Fe^{3+} , and Al^{3+} are all classified as hard acids (Lemire et al., 2013). The tendency of PO_4^{3-} to form complexes with the aforementioned metals as a function of pH is shown in Fig. 2.3. The figure shows the solubility of various phosphate minerals as a function of pH and phosphate concentration. The mineral that is closest to the intersection of the x and y axes at a given pH is the most chemically stable, and will consequently precipitate as the system reaches equilibrium. Depending on whether Fe or Al is present in a given system, along with an appropriate concentration of ligand, the iron phosphate mineral strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) or the aluminum phosphate mineral variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) will precipitate respectively until approximately pH 5.5. However, as the pH of the system increases above 5.5, the formation of several different Ca- PO_4^{3-} minerals is expected as the concentration of H_2PO_4^- is held constant. These relationships are important when assessing what kinds of fertilizer P reaction products may form in soils of differing pH, as evaluated chemically and spectroscopically in this thesis research.

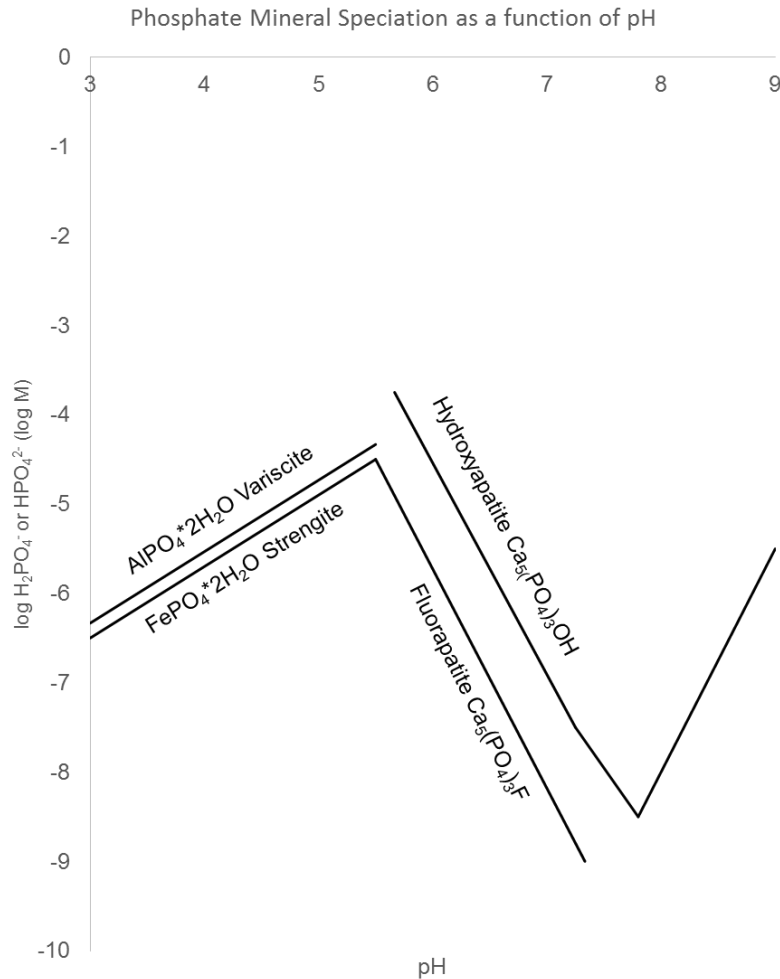


Fig. 2.3. Soil phosphate speciation as a function of orthophosphate concentration and soil pH (adapted from Havlin et al., 2014).

2.3 Soil Phosphorus Fertility

2.3.1 Phosphorus as a plant nutrient

Phosphorus is considered an essential nutrient for plant growth, involved in all metabolic processes requiring energy (Marschner, 1995). It is required for photosynthesis, nitrogen (N) fixation, flowering, fruiting, and maturation. Below ground the development of lateral roots and fibrous rootlets is promoted by P.

In soil, the average total P content of soil ranges from about 200 to 2000 kg P ha⁻¹ in the top 15 cm, and only about 5 to 10% of this P may be considered “labile” and readily available for plant uptake (Hinsinger, 1998; Hinsinger, 2001). When soluble forms of inorganic P are added to

the soil, they become fixed and, over time, become converted to insoluble compounds such as apatites in calcareous soils (Lindsay et al., 1979; Vu et al., 2008). Inorganic P (P_i) transformed into P_o by biological uptake can be mineralized back to soluble P by soil microbial processes or plant root exudates such as phosphatase enzymes, but may be held in recalcitrant organic forms in humus for many years. Given these natural limits on soil P fertility, P often has to be applied to the soil, either in the form of animal manure or synthetic fertilizer (Raghothama and Karthikeyan, 2005; Richardson 2009) to supplement the indigenous soil supply of P in order to supply sufficient P for optimum plant growth.

2.3.2 Soil phosphorus forms present in an agroecosystem

Large amounts of chemically stable forms of P may accumulate in a soil receiving regular additions of fertilizer P. In fact, depending on the nature of soil and crops grown, crop utilization of P rarely exceeds 20% of the applied P in the year of application (Reddy et al., 1999). The biologically active forms of P, at least in the short term, that accumulate in soil appear to be in classes operationally defined as labile inorganic P ($\text{NaHCO}_3\text{-}P_i$) and moderately labile organic and inorganic forms ($\text{NaOH-}P_o$ and $\text{NaOH-}P_i$) (Reddy et al., 1999). Phosphorus is highly reactive in soil, and its retention in soil is a function of soil concentrations of clay, organic carbon, and exchangeable Ca and Magnesium (Mg) (Ige et al. 2005). In particular, P_i forms not utilized by plants are readsorbed to soil components in the form of strongly adsorbed fractions, while accumulation of P_o forms may be attributed to biological and biochemical immobilization (Hedley et al., 1982; McGill and Cole, 1981). However, these temporarily unavailable P forms may become available to crops in subsequent years through chemical solubilisation and biological mineralization (Halvorson and Black, 1985). In this thesis research, chemical techniques (Hedley et al., 1982) are used to separate soil P into different fractions. As well, spectroscopic information obtained through P XANES is used to elucidate the effect that fertilizer application method has on influencing soil P_i speciation in an agroecosystem, while ^{31}P NMR spectroscopy is employed to investigate the effect on P_o species (See Appendix A).

P_o compounds in soil represent a source of appreciable quantities of orthophosphate ions which are released into the soil solution through the process of mineralization. Although the degree to which P_o mineralization occurs varies widely among soils, researchers have reported plant available P contributions of 5 to 7 kg ha⁻¹ yr⁻¹ from mineralization of P_o compounds

(Tisdale et al., 1993). In some soils the P_o fractions can be significant. For example, the P_o fraction made up approximately 60 to 73% of the total P pool in the A horizons of three Saskatchewan soils, even 60 to 70 years after cultivation of native land (Tiessen et al., 1982). Compared to thirty or forty years ago, improved techniques for identification and quantification of P_i and P_o compounds are available to better reveal the forms and behaviour of P in soil.

2.4 Soil Phosphorus Measurement Techniques

2.4.1 Chemical extraction methods

Methods of chemical extraction to determine concentrations of soil P aim at extracting a certain percentage of total soil P. These methods do not provide true measures of P that will be taken up by the plant, but rather provide a proxy of plant available P. Regression equations created from fertilizer response experiments are used to develop these relationships (Tiessen and Moir, 2008). One such chemical extraction method was outlined by Ashworth and Mrazek (1995), known as the Modified Kelowna (KM) method, which aims to provide a measure of plant available P. Satisfactory correlations between plant available P, as predicted by the KM method, and actual plant uptake have been previously demonstrated ($r^2 = 0.76$). Further, these authors showed that P extracted by this method and the popular Olsen method were strongly positively correlated ($r^2 = 0.92$) (Qian et al., 1994). Additionally, this method has been shown to be effective for use on calcareous soils that are common on the Canadian Prairies, as the extraction is conducted at a pH that is able to neutralize the buffering capacity of these soils (Ashworth and Mrazek, 1995). Other chemical extraction methods for soil P described later in this thesis include a sequential chemical extraction (Tiessen and Moir, 2008) and a water soluble P extraction (Sharpley et al., 2008).

2.4.2 Anion exchange resin membranes

Additionally, ion exchange resins may be used to assess a soil's nutrient status, by acting as a sink for a given nutrient ion during a certain period of extraction (Qian and Schoenau, 2002). In one application of this technology, a resin membrane is encapsulated within a plastic frame, thereby creating a probe which may be inserted in soil. These resin membranes carry an electrostatic charge which is neutralized by a particular counterion of opposite charge. Cation-exchange resins are created with sulfonic acid functional groups, while anion exchange resins

possess tertiary ammonium functional groups (Qian et al, 2008). When these probes are placed in situ in a soil environment, a diffusion-sensitive system is created, where ions adsorbed to the resin membrane will exchange with appropriately charged ions in the soil solution, or adsorbed to soil minerals, until chemical equilibrium is achieved. Therefore, as this method accounts for rates of release of ions bound to various soil surfaces, as well as the rate of diffusion through bulk soil, it is considered an effective method of assessing the rate at which nutrients may be potentially supplied to a plant's root, known as Nutrient Supply Rate (Qian and Schoenau, 2002). Myers et al. (2005) provided further support for the validity of this method, by developing regression equations of extractable P by the Olsen-P method on extractable P by resin membrane ($R^2 = 0.96$). Further, researchers have shown that P supply rate assessed by resin membranes correlate well with P uptake and P concentration of plant biomass (Khatiwada et al., 2012).

Advantages of the use of resin membranes to assess soil P supply rate are that they provide a measure of P that is potentially available for plant uptake, by accounting for nutrient release from soil surfaces and diffusive transport through the bulk soil (Qian and Schoenau, 2002). Secondly, resin membranes have been touted as a cost effective method of assessing soil P supply, owing largely to the re-useable nature of the membranes. In fact, Schoenau and Huang (1991) reported the use of a single resin probe as many as 500 times without a reduction in efficacy of results or causing physical damage to the probe. Finally, this method is advantageous given that it is suitable for assessing soil P supply rate of soils of varying physical and chemical conditions, as this test is conducted at the soil's inherent pH (Qian and Schoenau, 2002). On the other hand, P supply rate is a function of soil moisture and temperature, and caution must be exercised when comparing supply rates obtained from soils of varying environmental conditions. This variation in P supply rate under changes in soil temperature or moisture would also be experienced by a plant, however. A second perceived disadvantage relates to the units in which nutrient supply rate is reported. This measure is reported as an amount of nutrient per unit of membrane surface area per time of soil exposure (e.g. $\mu\text{mol P cm}^{-2} \text{ h}^{-1}$), whereas traditional chemical extractions report results as mass of nutrient per mass of soil (e.g. mg P kg soil^{-1}). This is disadvantageous, as no simple method exists for converting results obtained between the different units. However, this limitation is less of an issue with elements such as P and potassium (K), where traditional chemical extraction procedures provide an index of nutrient availability rather than an absolute measure (Qian and Schoenau, 2002).

2.4.3 Spectroscopic techniques

2.4.3.1 X-Ray absorption near edge structure

X-Ray Absorption Near Edge Structure is a spectroscopic technique which measures energy released from atoms excited by x-rays. This method is increasingly being used to investigate P speciation in soil samples and has been shown to differentiate adsorbed from precipitated phases of P (Hesterberg et al., 1999; Beauchemin et al., 2003; Sato et al., 2005). Further, P species, and the oxidation state in which they exist, may be identified with great specificity due to each species having unique spectral features, commonly known as fingerprints, located in the XANES region (Hesterberg et al., 1999; Khare et al., 2004; Peak et al., 2002). For example, researchers have shown that Fe-phosphate compounds have a characteristic pre-edge spectral feature within the energy range of 2144 to 2147 Electron Volts (eV). Conversely, a distinct spectral “shoulder” has been observed within an energy range of 2151 and 2155 eV for calcium phosphate minerals. Finally, a minor pre-edge inflection has been observed for aluminum phosphate minerals at approximately 2148 eV. These unique spectral features may be used in combination with linear combination fitting and principle component analysis to compare the spectra of an unknown sample with a set of known standard spectra (Khatriwada et al., 2012). In addition to the specificity of XANES for elucidating P speciation, this technique may be considered an in-situ method, allowing speciation to be determined at the soil’s inherent pH (Toor et al., 2006). However, it has been noted that determining P speciation with the use of XANES is effective only if the spectral features of a given compound are clearly distinct from other compounds of the same element or of another element having a similar spectral feature (Ajiboye et al., 2007).

2.4.3.2 ³¹P-Phosphorus nuclear magnetic resonance spectroscopy

Nuclear Magnetic Resonance techniques exploit the fact that certain nuclei, such as ³¹P, possess an odd number of protons and neutrons when summed, thereby behaving as a magnetic dipole. Upon application of a radio-frequency pulse, the ³¹P nucleus will absorb, and subsequently emit, energy and the emitted energy will be detected and recorded as a peak. Nuclear Magnetic Resonance is effective as a spectroscopic technique, as any given nucleus will be shielded to a certain degree from the applied radio frequency by the electron cloud of the

molecule in which the nucleus is located. This shielding factor influences both the amount of energy required for a nucleus to resonate and the amount of energy emitted. Therefore, a peak will be recorded at a specific position in a spectrum based on the chemical bonds that the nuclei participates in (Cade-Menun, 2005b). Further utility of this spectroscopic technique is that it may be used to quantitatively identify the various P compounds in a sample, as the intensity of the peak detected from the emitted energy is proportional to the total number of all the different P nuclei that are releasing energy (Cade-Menun, 2005a). Before conducting a ^{31}P NMR experiment, one must decide whether it will be conducted on a solid sample (solid-state ^{31}P NMR) or on an extract (solution ^{31}P NMR), each with their associated advantages and disadvantages, as described below. A complete description of the two sample types is out of the scope of this review, but is described in great detail elsewhere (Cade-Menun, 2005ab).

As with other soil P assessment techniques, there are inherent advantages and disadvantages associated with the use of ^{31}P NMR. First, ^{31}P represents the only naturally occurring P isotope in the soil environment, which allows for the potential detection of all P species in a sample. This fact allows for the detection of a wide range of P_o and P_i bearing compounds generally of interest in environmental studies, such as phosphonates, orthophosphate, orthophosphate monoesters, orthophosphate diesters, pyrophosphate, and polyphosphate (Cade-Menun, 2005a). Further, this technique, particularly solid-state ^{31}P NMR, is touted as a non-invasive spectroscopic technique which requires minimal sample preparation (Cade-Menun, 2005b). However, it should be noted that a minimal concentration of $1 \text{ mg P g soil}^{-1}$ is required for proper signal detection, thereby limiting the effectiveness of this technique on soils of low P content (Magid et al., 1996). Further, the resolution of spectra obtained from solid-state ^{31}P NMR is much poorer than that obtained from solution ^{31}P NMR. On the other hand, solution ^{31}P NMR results in the production of spectra with greater resolution and overcomes the limitations associated with soils of low P concentration due to a post-extraction concentration procedure (Cade-Menun, 2005b). Of the many potential extractants (sodium hydroxide (NaOH), the commercially available chelating resin ChelexTM in water, NaOH mixed with ChelexTM, NaOH mixed with sodium fluoride (NaF), and NaOH mixed with ethylenediaminetetraacetic acid (EDTA) there are inherent limitations associated with each due to the risk of hydrolysis of P_o , and uncertainty as to which extractant is most appropriate to be used (Cade-Menun, 2005a).

2.5 Phosphorus Fertilizer Management Considerations

2.5.1 Phosphorus fertilizer application methods

Phosphorus is considered an essential element for plant growth and development (Raghothma and Karthikeyan, 2005; Richardson, 2009; Chiou and Lin, 2011). Due to the low plant availability of P in soil, it is often applied in the form of inorganic fertilizer, or as a component of animal manure. There are several different methods in which fertilizer P may be applied to a soil including seed placed application, placement in a deep band, and broadcast application. Placement of small amounts of fertilizer P in the immediate vicinity of the seed has been shown to improve the early growth of seedlings particularly when soil temperature and/or nutrient status of the soil is low compared to no fertilizer application, or placement in a separate band (Kristoffersen et al., 2005; Marschner, 1995). The above factors have been found to limit the availability of nutrients by a reduced rate of diffusion (Barber, 1995), a reduction in plant uptake kinetics (Bravo-F & Uribe, 1981) and a reduction in soil mineralization rate (Kristoffersen et al., 2005). According to Kristoffersen et al. (2005), the increased uptake of P and increased crop yield from the application of seed-placed starter fertilizer was larger early in the growing season compared to later. For example Monoammonium Phosphate (MAP) application at a rate of 20 kg P₂O₅ ha⁻¹ resulted in increased P uptake of 38% at the period of the third leaf extension, 8% at the period of the first visible awns, and 8% at maturity compared to the control treatment that had not received seed-placed fertilizer P in spring wheat. Several factors have been noted, that determine if the early growth benefits from starter fertilizer application persist to maturity. These factors include variations in the release of soil mineral N under various soil conditions, the influence of soil water content on the availability of residual P, and the interaction between water supply and growth (Kristoffersen et al., 2005).

Similarly, differences exist in P uptake when fertilizer is applied in a band as compared to broadcast application. Placement of fertilizer in a band reduces the total surface area of contact between soil and fertilizer. Researchers have shown that this factor causes a reduction in soil immobilization. Due to this reduced rate of immobilization, the fertilizer P remains in a form that is more readily available for longer periods of time compared to when it is mixed throughout the soil (Barber, 1995). Therefore, in addition to the anticipated yield benefits from banded P application compared to broadcast application, it has been hypothesized that broadcast

application of fertilizer P with incorporation will result in increased uptake of P compared to broadcast application without incorporation, due to the limited mobility of P in cold, dry soil.

2.5.2 Considerations for seed-placed fertilizer phosphorus

Although the greater yield response from seed-placed fertilizer P relative to broadcast application under certain conditions are widely known, there are limits to how much fertilizer P may be safely applied with the seed (Government of Saskatchewan, 2012; Havlin et al., 2014). Sensitivity to seed-placed MAP is due to osmotic effects, where salt concentration in the soil solution outside of the plant root is greater than the concentration in the root. Diffusion causes water to flow outside of the cell due to the concentration gradient, ultimately resulting in symptoms to the plant resembling drought stress (Havlin et al., 2014). Further, as ammonium in MAP is oxidized to nitrate (NO_3^-), via nitrification, plant roots may be temporarily exposed to nitrite, which is toxic (Brady and Weil, 2008). This limitation on the recommended amount of fertilizer P to be applied with the seed may result in significant soil P depletion following a season of crop growth under conditions of optimal yield, as certain crops are able to take up more soil P than may be safely applied (Grant, 2012). The incorporation of increasingly popular crops into a rotation that are sensitive to high rates of seed-placed fertilizer P, such as soybean and canola, further exacerbate this problem. In the case of soybean and canola, assuming a yield of 2695 kg ha^{-1} , a net decrease of 24.6 and 22.4 kg soil P ha^{-1} , respectively will result if recommended seed-placed rates of fertilizer are adhered to (Table 2.1).

Table 2.1 Balance between seed-placed P addition and P removal for various crops grown on the Canadian Prairies (adapted from Grant (2012)).

Crop	Yield (kg ha^{-1})	Seed Limit (kg ha^{-1})	Removal (kg ha^{-1})	Net Effect (kg ha^{-1})
Soybean	2695	11.2	35.8	-24.6
Canola	2695	22.4	44.8	-22.4
Wheat	2695	56	32.5	+23.5

2.5.3 Environmental implications of phosphorus fertilizer application methods

In the Canadian Prairies, the spring runoff period has been identified as a critical period for the addition of Dissolved Reactive P (DRP) to water bodies, with 45% of the flow from the

Lake Winnipeg watershed into Lake Winnipeg taking place from April to July. Several factors influence runoff flux from an area. One study in Manitoba indicated that DRP load was significantly greater in a clay loam textured soil compared to a sand textured soil due to the greater runoff volumes generated in the clay loam soil compared to the sand (Kumaragamage et al., 2009). Phosphate in surface water can induce the process of eutrophication. Eutrophication is a condition brought about by excessive growth of algae and aquatic weeds in a body of water (Carpenter et al., 1998). This process is largely brought about by increasing P concentration in water, which is often a limiting nutrient for algal growth (Schindler, 2006; Carpenter, 2008). In addition to excessive amounts of bioavailable P, algal growth is promoted by warm water temperatures. When the algae die and settle on the bottom of an aquatic ecosystem, they are decomposed by bacteria, resulting in the consumption of oxygen from the surrounding water. Oxygen depletion leads to the death of fish and other aquatic organisms.

Dissolved P is the major form of P loss occurring under natural field conditions on the Canadian Prairies (Sheppard et al., 2006; Little et al., 2007; Cade-Menun et al., 2013). Dissolved forms of nutrients are readily taken up by simple organisms and consequently have the greatest potential impact on water bodies (Lang et al., 2013). Levels of soil test phosphorus in surface soils have been directly linked to the balance between phosphorus added and removed in crop harvest and to the P export in runoff (Stumborg and Schoenau, 2008).

Repeated broadcast application of fertilizer P results in enriched soil test P levels in the surface soil due to a lack of incorporation of the fertilizer as well as a return of nutrients to the soil surface from decomposed plant residue (Buah et al., 2000). Farmaha et al. (2012) observed increases in soil test P levels of 26 mg P kg⁻¹ in the top 5 cm of soil from the broadcast application of 36 kg P ha⁻¹ yr⁻¹ over a 3 year period compared to the control treatment, with an increase in soil test P levels of only 7 mg P kg⁻¹ in the top 5 cm of soil from the deep banded application of P at the same rate and over the same time period. Therefore, banded fertilizer P application has been suggested as an effective way to supply P to the soil without significantly increasing surface STP levels (Fernandez and Schaefer, 2012). This is relevant in light of the environmental risk that enriched STP concentration in the surface soil poses, as greater dissolved P concentrations and loads in runoff water were observed from broadcast fertilizer P application compared to when fertilizer P was incorporated into the soil in Illinois, USA (McIsaac et al.,

1995). The research in this thesis examines for the first time the effect of P fertilizer placement and rate on DRP in snowmelt runoff from a Canadian prairie soil.

3. EFFECT OF PHOSPHORUS FERTILIZER METHOD AND RATE OF APPLICATION ON SOIL PHOSPHORUS STATUS, GROWTH, AND UTILIZATION BY SOYBEAN AND FABA BEAN

3.1 Preface

Annual applications of fertilizer or manure P in excess of crop removal can result in agricultural soils becoming enriched in soluble, labile P. On the other hand, the inclusion of high P demanding crops in rotation that are also sensitive to seed-placed fertilizer P may lead to a depletion of soil available P, as annual crop removal of soil P exceeds what can be safely applied with the seed. Agronomic crop and soil responses to P fertilization are reported on in Chapter 3. Two studies are covered in Chapter 3. In the first study, conducted in the field, a total of seven treatments including four different fertilizer application methods and three application rates, were evaluated for their effect on soybean yield, phosphorus uptake in grain and straw, and residual soil nutrient levels. The second study was conducted in a controlled environment, where soybean and faba bean were grown under conditions where seed-placed fertilizer P was applied at five application rates and the effect on germination and early growth determined. The following Chapter 4 deals with assessing the fate of residual fertilizer P in the soil. Chapter 4 covers a detailed examination of spatial distribution of residual fertilizer P as influenced by placement and rate, mobility of P in a simulated snowmelt run-off study, and a crop residue phosphorus release experiment. Additionally, XANES spectroscopy was conducted on soil samples collected from the site to assess the effect that fertilizer P application method has on influencing soil P speciation.

3.2 Abstract

In general, a lack of understanding exists regarding the response of short-season soybean to P fertilization on the Canadian prairies. Increased interest has recently been shown by agricultural producers in broadcast fertilizer applications, largely as a time-saving mechanism. A field study was conducted in a field in south-central Saskatchewan (Brown Chernozem, Echo Association) where soybean was grown with seed placed, banded below seed, and broadcast mono-ammonium phosphate fertilizer application methods. Rates were 20 kg P₂O₅ ha⁻¹ for all placement methods along with additional rates of 40 and 80 kg P₂O₅ ha⁻¹ for broadcast treatments and a control without fertilizer P added. Two sites within the same field were chosen to reflect differences in slope position: Downslope and Upslope. At the Downslope position, application of fertilizer P in a band below the seed resulted in a greater soybean grain yield compared to the control treatment or broadcast application at three rates (20, 40, and 80 kg P₂O₅ ha⁻¹) ($P < 0.10$). Application in a band or with the seed also resulted in significantly lower water soluble P concentrations in the surface soil layer (0 to 5 cm) compared to broadcast P application. Water soluble P is known to be an effective predictor of off-site transport of applied P in runoff water.

The incorporation of crops sensitive to high rates of seed-placed fertilizer P, such as soybean, may result in soil P depletion, as the crops typically take up more soil P than can be safely applied with the seed. A pot study was conducted in a controlled environment to examine the effect that varying rates of seed-placed fertilizer P (0, 20, 40, 60, and 80 kg P₂O₅ ha⁻¹) has on soybean seedling germination and emergence, as well as biomass production measured 14 days after sowing. Application of seed-placed fertilizer P at rates in excess of 20 kg P₂O₅ ha⁻¹ caused a significant reduction in soybean seedling germination and emergence compared to the control treatment. However, only the highest rate of seed-placed fertilizer P (i.e. 80 kg P₂O₅ ha⁻¹) caused a significant reduction in soybean biomass production relative to the control.

3.3 Introduction

Soybean (*Glycine max* (L.)) is a crop receiving more attention than in the past from agricultural producers of the Canadian prairies, as evidenced by the increasing number of hectares that have been recently devoted to its production, especially in Manitoba (Risula et al., 2015a). In Saskatchewan, soybeans were sown on 68,800 ha in 2013 and this value was anticipated to increase in 2014, although data was not available at the time of publication (Statistics Canada, 2015). Few fertility management studies have been conducted with short season soybean on the Canadian prairies. Specifically, there is a need to examine the soil and plant responses to P fertilization of short-season soybean, as ample P supply is critical for maximizing yield of grain legume crops and crops that follow in rotation. Additionally, there has been increased interest among agricultural producers on the Canadian prairies in the broadcast application method of fertilization as a time saving mechanism compared to in-soil fertilizer placement (Lyseng, 2014). The objectives of the work described in this chapter were to evaluate soybean response to P fertilizer management, including placement and rate. Therefore a study was conducted in 2014 on a typical farm field in south-central Saskatchewan to evaluate the effect that mono-ammonium phosphate fertilizer application method has on soil and plant P in a short-season soybean variety crop. In addition to documenting important agronomic attributes such as crop yield response, phosphorus uptake and removal in harvested grain, the effect that fertilizer application method has on soybean P uptake and content in straw is assessed, as P concentration of crop residues is known to influence the amount of orthophosphate in leachate water passing through crop residues (Cermak et al., 2004). Soil cores were collected after crop harvest to determine residual soil P. An understanding of this is required to evaluate the effect of placement on potential losses of P in surface and subsurface water run-off. For example, broadcast fertilizer P application has been shown to cause enrichment of soil P near the soil surface (Borges and Mallarino, 2000). This enrichment of soil P near the soil surface is anticipated to promote off-site transport of P in run-off water.

Limited research has been conducted on the Canadian prairies to determine the optimum rate and placement strategy of fertilizer P for soybean growth (Bardella et al., 2015). In-soil placement of fertilizer P in a band is the recommended application strategy on the Canadian prairies (Grant, 2012), though for soybean, application rate is not recommended to exceed 20 kg P₂O₅ ha⁻¹ when fertilizer P is placed with the seed (Risula et al., 2015b.). This may lead to

significant soil P depletion, as crop uptake may exceed P input (Grant, 2012). In addition to the yield benefits from in-soil placement of fertilizer P compared to broadcast application, broadcast fertilizer P application has also been shown to lead to significant soil P enrichment near the surface (Borges and Mallarino, 2000) where it is susceptible to loss in run-off. Therefore, an experiment was conducted to determine the effect that seed placed fertilizer P application at higher than the 20 kg P₂O₅ ha⁻¹ recommended seed-row placed rate (i.e. 2x, 3x, and 4x) has on soybean seedling emergence and biomass production under controlled environmental conditions. Faba bean was also grown under the same conditions for comparison, as faba bean is a grain legume believed to be quite tolerant to high rates of fertilizer P placed in the seed-row.

3.4 MATERIALS AND METHODS

3.4.1 Field Study

3.4.1.1 Site description

The study site (legal location SE32-21-4-W3) was situated approximately 1 km north of Central Butte, Saskatchewan, within the Brown soil zone, having a loam to clay loam texture, and classified as an Orthic Brown Chernozem according to the Canadian System of Soil Classification (Soil Classification Working Group, 1998). The soil map unit in which the site is situated describes the site as consisting predominantly of soils of the Echo association (Ayres et al., 1985). The soils of this site have been formed on glacial till parent material, having a gently sloping topography and classified as slightly stony. To determine the influence of variation in physical and chemical soil characteristics on crop growth, P speciation, and concentration in collected soil and runoff water, two sites representing contrasting slope positions in the same field approximately 50 m apart were chosen, herein referred to as the Downslope and Upslope locations. The name given for the two sites also reflects the change of elevation between them, where the Upslope site was situated at a higher elevation than the Downslope site, as indicated in (Fig. 3.1). The field was seeded to canola in 2012 and to spring wheat in 2013.

The experiment was conducted as a Randomized Complete Block Design with seven treatments each replicated four times. Soybean was grown in 2014. A single soil sample was collected with a hand held Dutch Auger for the purpose of initial site characterization from each of the control plots across the study area on May 8, 2014 (Table 3.1). Additional details of the sampling strategy employed are provided in section 3.4.1.2 below. According to soil test

analysis, the soil at both slope positions was deficient in P and sufficient in S and K and micronutrients (Fe, Cu, Mn, and Zn) for soybean production (ALS Labs, Saskatoon, SK).

Table 3.1 Summary of baseline soil properties in soil cores collected from the Downslope and Upslope field site locations in spring 2014. Values are means from analysis of eight individual soil cores collected in May from the marked out control plots before any treatments or field operations were conducted.

Depth				Soil Property			
	P [†]	N [‡]	S [§]	K [†]	pH [¶]	EC [#]	OC
(cm)	-----mg kg soil ⁻¹ -----					(dS m ⁻¹)	(%)
Downslope							
0-15	7.2	3.8	32.5	358	7.2	0.21	1.5
15-30	3.9	3.5	37.2	195	7.2	0.17	1.2
30-60	-	4.7	80.2	-	-	-	-
Upslope							
0-15	7.5	1.7	28.3	263	7.8	0.29	1.4
15-30	4.5	2.0	31.0	190	7.9	0.25	1.1
30-60	-	2.3	45.1	-	-	-	-

[†]P and K= Modified Kelowna extractable phosphate, PO₄-P and K (Qian et al., 1994).

[‡]N= CaCl₂ extractable nitrate, NO₃-N (Houba et al., 2000).

[§]S= CaCl₂ extractable sulphate, SO₄-S (Houba et al., 2000).

[¶]pH measured in a 1:2 soil:water suspension (Hendershot et al., 2008).

[#]EC measured in a 1:2 soil:water suspension (Miller and Curtin, 2008).

3.4.1.2 Initial soil sampling and post-harvest

Soil samples were acquired for baseline nutrient concentrations and soil properties of the site on May 8, 2014 before treatments were applied. Two cores from each replicate plot of the C and B(20) treatments were extracted with a hand held Dutch Auger and a sub-sample of the resulting composite for each plot was analyzed for various nutrients (extractable P, K, NO₃⁻, SO₄²⁻) in addition to selected chemical properties (pH, Electrical Conductivity, % Organic Carbon) at two depth increments (0 to 15 cm and 15 to 30 cm). Post-harvest soil sampling took place on September 18, 2014. A composite sample was obtained for each plot by collecting four cores within each plot from all treatments and combining the samples according to depth. A hydraulic punch truck fitted with a 5 cm diameter barrel was used to extract samples at four depth increments (0 to 5 cm, 5 to 10 cm, 10 to 30 cm, and 30 to 60 cm). Samples were placed in a fridge at 5°C until preparation for chemical analysis, which consisted of air drying samples at

30°C followed by grinding with a Wiley mill to ensure they pass a 2 mm sieve. After processing, the samples were stored at room temperature until chemical analysis.



Fig. 3.1. Photo taken from the Upslope position in the foreground, showing change in elevation leading toward the Downslope position in the background.

3.4.1.3 Outline of treatments

A total of seven treatments were applied in this experiment.

- 1) No P fertilizer, but ammonium chloride added to account for N in mono-ammonium phosphate (11-52-0). Abbreviated as (C) for control;
- 2) Phosphorus placed with seed in spring at 20 kg P_2O_5 ha⁻¹ as 11-52-0. Abbreviated as (SP) for seed placed;
- 3) Phosphorus pre-plant banded below the seed-row in spring at 20 kg P_2O_5 ha⁻¹ as 11-52-0. Abbreviated as (DB) for deep banded;
- 4) Phosphorus pre-plant broadcast in spring at 20 kg P_2O_5 ha⁻¹ as 11-52-0 with incorporation. Abbreviated as (B/I) for broadcast and incorporated;

- 5) Phosphorus pre-plant broadcast in spring at 20 kg P₂O₅ ha⁻¹ as 11-52-0 without incorporation. Abbreviated as B(20) for broadcast alone;
- 6) Phosphorus pre-plant broadcast in spring at 40 kg P₂O₅ ha⁻¹ as 11-52-0 without incorporation. Abbreviated as B(40) for broadcast alone at 40 rate; and
- 7) Phosphorus pre-plant broadcast in spring at 80 kg P₂O₅ ha⁻¹ as 11-52-0 without incorporation. Abbreviated as B(80) for broadcast alone at 80 rate.

Treatment 1 consisted of three sub-treatments to account for the varying rates of N in the MAP that were applied for the 20, 40, and 80 kg P₂O₅ ha⁻¹ rates.

3.4.1.4 Site preparation

The study site was prepared for seeding operations on May 12, 2014. Granular TagTeam™ inoculant (Novozymes BioAg) was broadcast across the entire study area at 9.6 kg ha⁻¹, which is twice the recommended application rate for 25 cm row spacing. The increased rate of inoculant application was performed as soybeans (and other legumes) had not been previously grown on the study area, and no native soybean rhizobial populations exist in Saskatchewan soils (Hnatowich, 2014). The inoculant was incorporated into the soil at an approximate depth of 7 cm using a light roto-till. Fertilizer was broadcast for treatments B(20), B(40), and B(80) at the appropriate rates, as described above, and a roto-tiller was used to incorporate the fertilizer at a depth of 7 cm for treatment B/I. For treatment DB, fertilizer P was applied in a band approximately 7.5 cm deep created by a hoe which was then covered back in manually with soil and which would be seeded over later. The garden hoe was used to create the furrow as this method ensured uniform depth of the banded fertilizer. Finally, the entire study area was rolled with a Push/Tow Poly Lawn Roller™ (Brinly-Hardy) to create a uniformly packed seed-bed to promote seedling establishment.

3.4.1.5 Field operations

Seeding

On May 20, 2014, prior to seeding, soybean (cv. NSC Moosomin) seeds were treated with Apron Maxx RTA™ (Syngenta) liquid fungicide at a rate of 325 mL per 100 kg seed (Syngenta Canada Inc., 2013). Granular *Rhizobium* inoculant was also mixed with the soybean

seed to provide twice the recommended rate of inoculant application for 25 cm row spacing (9.6 kg ha⁻¹) to ensure that sufficient populations of rhizobium were present in the soil at the time of sowing (Hnatowich, 2014). Soybean seeds and inoculant were then placed in a walk-in cooler for approximately 12 h until seeding commenced. Seeding operations took place on May 21, 2014, with the date chosen to ensure that soil temperature at the depth of seeding was 10°C (Hnatowich, 2014). The entire study area was seeded with a double-disk press drill at 25 cm spacing, for a total of three rows within each 3 m by 1 m plot and at a rate of 80 kg soybean seed ha⁻¹. Care was taken to ensure an approximate seeding depth of 1.25 to 1.9 cm, as recommended (Hnatowich, 2014). Soybean seeds were planted directly above the deep banded fertilizer for the DB treatment.

Weed control

Weed control within the study site was ensured through means of chemical control. Glyphosate was sprayed on May 21, 2014 at a rate of 2 L ha⁻¹ as well as on June 8, June 23, and July 8, 2014 at a rate of 0.66 L ha⁻¹ (540 g active ingredient per liter). Additionally, hand weeding was performed on June 3, 2014.

Climate data

Climate data was obtained from the nearest Environment Canada weather station (Elbow, Sk.) to the field site. Little variation between 2014 and 25 year average temperatures was noted. However, precipitation in 2014 was higher than the historical mean in all months except July.

Table 3.2 Comparison of mean monthly precipitation (mm) and temperature (°C) during 2014 growing season to 25 year (1990-2014) at Central Butte, Sk.

Month	Mean Monthly Temperature (°C)		Mean Monthly Precipitation (mm)	
	2014	HM [†]	2014	HM [†]
May	10.5	10.8	61.7	30.7
June	14.2	15.5	125.0	60.6
July	18.1	18.9	13.1	35.6
August	18.0	17.9	47.2	34.4
September	12.3	12.5	35.1	27.4

[†]HM= Historical mean (1990-2014).

Crop harvest

Harvest operations were conducted on September 18, 2014 after a killing frost occurred on September 11. A sub-sample of 1 m length and hand cut approximately 2.5 cm above ground was taken from the centre row of each plot row. Upon collection of the sub-sample, the remaining crop was hand cut at the same height and removed from the site for ease of soil sampling. Samples from each plot were placed in cloth bags, and allowed to air dry prior to threshing operations.

Crop processing

Soybeans were threshed on October 21, 2014. The grain was then cleaned on October 23 and October 24, 2014, and the resulting harvested grain and straw yields were measured and reported on a kg per ha basis. After harvest and grain cleaning, soybean straw was stored in cloth bags at room temperature (~21°C) until analysis of total P and water extractable P in crop residue. Finally, a subsample of soybeans collected from each plot was ground on November 14, 2014 with the Retsch ZM 200™ grinder and stored at room temperature until laboratory determination of grain nutrient content by acid digestion.

3.4.1.6 Laboratory analysis

Soil total organic carbon

The LECO-C632™ carbon analyzer (LECO Corporation) was used to measure total organic carbon (TOC) of soil samples taken from the study area. The methodology is based on previous research which has shown that during combustion at 1100°C, both organic and inorganic carbonates are evolved as carbon dioxide (Harris et al., 2001). For this reason, and as Saskatchewan soils generally contain appreciable quantities of inorganic carbonates, a Hydrochloric Acid (HCl) pre-treatment step was employed as described by Harris et al. (2001) to remove this as a confounding factor in the determination of TOC.

Soil phosphorus supply rate

The “Sandwich” test was employed to measure P supply rate, as outlined by Qian et al. (2008). Briefly, anion exchange membranes were prepared by soaking resin membranes in 0.5 M sodium bicarbonate (NaHCO_3) solution for a minimum of 2 h, and repeating the process for a total of four times. The solution was stirred periodically throughout the entire period. “Sandwiches” were prepared by placing subsamples of each soil into two Snapcap vial lids for each sample and adding deionized water until subsamples were brought up to field capacity. A single anion exchange membrane was then placed between two Snapcap lids filled with soil, ensuring good contact between the soil and membrane to form a “Sandwich” and the “Sandwich” sealed with Parafilm laboratory film. After a 24 h extraction period, membranes were removed and thoroughly washed in deionized water, taking care to ensure that all soil particles were removed. Membranes were then individually placed in a Snapcap vial (8.5 dram) filled with 0.5 M HCl. Samples were incubated for 1 h on a shaker set at 200 Revolutions Per Minute (RPM). After incubation, resin membranes were removed from the Snapcap vials, and the eluent was analyzed for orthophosphate content using Technicon automated colorimetry for phosphate in water and acid solutions.

Water soluble phosphorus extraction

The use of water as a soil P extractant serves as an effective proxy for the amount of P that may be released from soil during a run-off event, and is described in detail by Sharpley et al. (2008). In this procedure, 2 g of air-dried soil was weighed into a plastic extraction bottle. Distilled water (100 mL) was added and the resulting solution was shaken at 200 RPM for 1 h. The solution was immediately filtered through a Whatman No. 454 filter, followed by vacuum filtration through a 0.45 μm membrane filter. The resulting filtrate was measured for orthophosphate concentration using colorimetric spectrometry with colour development achieved by the Murphy and Riley method (Murphy and Riley, 1962). Total water-extractable soil P was calculated according to equation one below.

$$\begin{aligned} &\text{Water-extractable soil P (mg orthophosphate phosphorus kg soil}^{-1}\text{)} && [1] \\ &= [\text{Concentration of P in extract}] \times [\text{volume of extractant/mass of soil}] \end{aligned}$$

Plant available soil nitrate and sulfate extraction

Plant available soil nitrate (NO_3^- -N) and sulfate (SO_4^{2-} -S) were extracted according to established methods (Houba et al., 2000). The extracting solution (0.01 M CaCl_2) was made by dissolving 1.11 g of Calcium Chloride (CaCl_2) in 1 L of distilled water. A sub-sample of 20 g of air-dried soil was weighed into a plastic extraction bottle and 40 mL 0.01 M CaCl_2 solution was added to each bottle. The resulting solutions were shaken for 30 min at 142 RPM on a rotary shaker. After shaking, the suspension was filtered through a Whatman No. 42 filter paper and refrigerated until analysis for soil NO_3^- and SO_4^{2-} by Atomic Absorption-Flame Emission spectrometry.

Plant available phosphate and potassium extraction

The Modified Kelowna extraction procedure was used to extract plant available orthophosphate and potassium (K^+). Briefly, 30 mL of Kelowna solution (Acetic Acid, Ammonium Acetate, and Ammonium Fluoride) was added to approximately 3 g of air dried soil. Samples were then shaken horizontally on a rotary shaker for 5 min at 142 RPM. After shaking, samples were filtered through VWR 454 filter paper, and the filtrate was stored at 5°C until analysis by AA-FE spectrometry.

Acid digest of soybean plant material

An acid digest of ground soybean grain and straw was conducted according to the method of Thomas et al. (1967). Briefly, 0.25 g of finely ground soybean grain or straw was weighed into glass digestion tubes and 5 mL of concentrated (conc.) sulfuric acid (H_2SO_4) was added. Samples were placed on a digestion block at 360°C for 30 min. Following this, samples were removed from the digestion block, allowed to cool, and 0.5 mL H_2O_2 was added. Samples were then placed on the digestion block an additional three times for 30 min, adding H_2O_2 after each heating period. Finally, samples were placed on the digestion block for 1 h. After samples were allowed to cool, distilled water was added to dilute the final volume of the sample to 75 mL to achieve a final concentration within the detection limit of the instrumentation. Samples were placed in a refrigerator until analysis for NH_4^+ , NO_3^- , and PO_4^{3-} by Technicon automated colorimetry.

3.4.1.7 Statistical analyses

Statistical analyses were conducted using PROC MIXED of SAS, Version 9.3 (SAS Institute Inc, 2012). This study was conducted as a RCBD with a total of seven treatments with four replicates. An ANOVA was conducted, with treatments as a fixed effect and block as a random effect. PROC UNIVARIATE was used to determine if the residual and block effect data were normally distributed. As a more rigorous statistical technique, where necessary, certain treatments were grouped into fertilizer application methods, and orthogonal contrasts between methods were conducted using PROC MIXED. PROC UNIVARIATE was used to determine if the measured values of a treatment were normally distributed. The Folded Form F statistic was utilized to determine if variances were equal. Where applicable, multi-treatment comparisons were conducted using the Tukey Test, and employing the Honestly Significant Difference (HSD) method. Additionally, individual comparisons of treatments were conducted using PROC TTEST. All tests were declared significant at the 10% level.

3.4.2 Controlled environment study

3.4.2.1 Soil description

The soil used in the controlled environment experiment was collected from the Downslope position of the same site as described in Section 3.4.1 above. Soil was collected from the site on September 29, 2013. Once brought back to the laboratory, the soil was air dried and thoroughly mixed to ensure homogeneity.

3.4.2.2 Experimental design

An experiment performed in a controlled environment was conducted to assess the effect of varying rates of seed placed fertilizer P on crop emergence and biomass production. This experiment was conducted as a CRD with four replicates. Soybean (*Glycine max* (L.)) (var. NSC Moosomin) and Faba Bean (*Vicia faba*) (var. CDC SSNS1), for comparison, were grown for two weeks, and the treatment effect on crop emergence and biomass production after two weeks was assessed. The crops were grown in trays divided into three experimental compartments, each

measuring 20 cm wide by 20 cm long by 15 cm deep. A total of five treatments, outlined below, were used in this experiment.

3.4.2.3 Outline of treatments

The treatments used are described below, followed by the abbreviation that is used to denote the treatment throughout the thesis.

- 1) Seed placed P at 0 kg P₂O₅ ha⁻¹. Abbreviated as C for control;
- 2) Seed placed P at 20 kg P₂O₅ ha⁻¹ as 11-52-0. Abbreviated as SP(20) for seed-placed 20;
- 3) Seed placed P at 40 kg P₂O₅ ha⁻¹ as 11-52-0. Abbreviated as SP(40) for seed-placed 40;
- 4) Seed placed P at 60 kg P₂O₅ ha⁻¹ as 11-52-0. Abbreviated as SP(60) for seed-placed 60; and
- 5) Seed placed P at 80 kg P₂O₅ ha⁻¹ as 11-52-0 Abbreviated as SP(80) for seed-placed 80.

3.4.2.4 Seeding Operations

Seeding operations commenced on January 6, 2015. Two kg of soil was weighed into each experimental compartment, for a total of 6 kg of soil per tray, and the soil was levelled to create a firm, even seed bed. A furrow, measuring 2 cm wide and 2.5 cm deep, was made in the middle of each experimental compartment along its entire 20 cm length. Fertilizer P at the appropriate rate was evenly spread along the length of the furrow for each treatment. Soybean seeds were treated with Apron Maxx RTATM (Syngenta) liquid fungicide at a rate of 325 mL per 100 kg seed (Syngenta Canada Inc. 2013). NodulatorTM inoculant (BASF) was applied to the compartments that were seeded to soybean at 9.6 kg ha⁻¹ for 20 cm row spacing by spreading evenly along the entire length of the furrow. Similarly, Nodulator XLTM *Rhizobium* inoculant for faba bean was applied in the same furrow to the compartments seeded to faba bean at 9.6 kg ha⁻¹ according to commonly practiced protocol (Crop Development Centre, personal communication, 2014). A total of 10 seeds were then placed along the length of the furrow, with the number of seeds chosen so that seedling emergence was able to be effectively quantified. Fertilizer, seed, and inoculant were then covered with approximately 2.5 cm of soil.

3.4.2.5 Soil moisture holding capacity

Soil moisture holding capacity was determined by taking a total of eight plastic vials (8 dram) with a porous bottom that were filled with soil to be used in the controlled environment experiment. The side of the vial was gently tapped during filling to ensure that soil was tightly packed. The vials were placed in an aluminum tray that was filled with approximately 1 cm of water. After waiting until soil saturation occurred (approximately 5 min) the vials were removed from the aluminum tray and placed on a paper towel for 5 min to allow free water to drain. Soil moisture holding capacity was then calculated according to equation two below.

$$\text{Soil Moisture Holding Capacity (\%)} = \frac{\text{mass of wet soil(g)} - \text{mass of dry soil (g)}}{\text{mass of dry soil (g)}} \times 100 \quad [2]$$

3.4.2.6 Environmental conditions

The experiment was conducted in light trays that were constantly illuminated with Grow-Lux™ lights at a constant temperature of 21°C. Plants were watered daily to ensure that soil was maintained at 75 % of the soil moisture holding capacity, which was 33.7% moisture by weight. To account for variability in environmental conditions within the light unit, the trays were randomly repositioned within the light unit weekly.

3.4.2.7 Harvest

Seedling emergence was assessed in each experimental compartment two weeks after seeding. Two weeks after seeding, the plants in each experimental compartment were cut at the soil surface, and placed in an oven for 48 h at 40°C to dry. Once plants were dried, the above ground biomass was weighed for each experimental compartment.

3.4.2.8 Statistical analyses

Statistical analyses were conducted using PROC MIXED of SAS, Version 9.3 (SAS Institute Inc, 2012). This study was conducted as a CRD with a total of five treatments in replicates of four. An ANOVA was conducted, with treatments as a fixed effect. PROC UNIVARIATE was used to determine if the residual data were normally distributed. Where

applicable, multi-treatment comparisons were conducted using the Tukey Test, and employing the Honestly Significant Difference (HSD) method. All tests were declared significant at the 10% level.

3.5 RESULTS

3.5.1 Field Study

3.5.1.1 Soil nutrients

Soil test extractable, available P contents in soils collected at both slope positions in fall 2014 after soybean harvest are presented in Tables 3.3 and 3.4. The different soil P tests followed similar patterns according to treatment, with the 40 and 80 kg P₂O₅ ha⁻¹ rates having higher residual soil available P than the control and no significant differences among placement methods for the 20 kg P₂O₅ ha⁻¹ rates and the control. Only the KM extraction showed a treatment effect at depth, with higher KM P (10 to 30 cm depth) in the B(40) and B(80) rate treatments than the other treatments. Soil test P was highest in the surface 0 to 5 cm and decreased with depth. In the Upslope position (Table 3.4), the mean values for each treatment revealed a similar pattern to the Downslope position as related to treatment effects, but significant effects were fewer, owing to greater variability among replicates in the Upslope site.

Table 3.3 Soil test P values from 3 tests for the Downslope position sampled in fall 2014 after soybean harvest. Values are means of soil cores collected from the four replicates of each treatment. Values within a row followed by a different letter are significantly different ($P < 0.10$). Tukey's Honestly Significant Difference method was used for multi-treatment comparisons.

	Depth (cm)	Treatment [†]							<i>P</i> Value
		C	SP	DB	B/I	B(20)	B(40)	B(80)	
		-----mg kg ⁻¹ -----							
KM	0-5	10.9 ^c	12.9 ^{bc}	16.9 ^{abc}	17.3 ^{abc}	12.7 ^c	23.0 ^{ab}	25.8 ^a	0.0009
P [‡]	5-10	3.1 ^a	3.5 ^a	3.8 ^a	4.3 ^a	3.3 ^a	4.4 ^a	4.4 ^a	0.0951
	10-30	1.8 ^b	1.8 ^b	2.2 ^{ab}	1.9 ^b	1.8 ^b	2.5 ^a	2.3 ^{ab}	0.0046
H ₂ O	0-5	5.0 ^c	5.8 ^c	6.7 ^{bc}	8.1 ^{abc}	5.5 ^c	11.0 ^{ab}	11.9 ^a	0.0010
Sol.	5-10	2.4 ^a	2.4 ^a	2.8 ^a	2.9 ^a	2.2 ^a	2.4 ^a	2.9 ^a	0.3317
P [§]	10-30	1.5 ^a	1.5 ^a	1.7 ^a	1.6 ^a	1.5 ^a	1.9 ^a	1.8 ^a	0.3673
		-----µg cm ⁻² -----							
	0-5	0.4 ^c	0.6 ^c	0.7 ^c	1.0 ^{bc}	0.5 ^c	1.7 ^a	1.9 ^a	<0.0001
Resin	5-10	0.1 ^a	0.1 ^a	0.1 ^a	0.2 ^a	0.2 ^a	0.1 ^a	0.2 ^a	0.1792
P	10-30	0.1 ^{ab}	0.1 ^{ab}	0.1 ^{ab}	0.1 ^a	0.1 ^{ab}	0.0 ^b	0.0 ^b	0.0073

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

[‡]KM P= Modified Kelowna Extractable P

[§]H₂O Sol P= Water Soluble P

Table 3.4 Soil test P values from 3 tests for the Upslope position in fall 2014 after soybean harvest. Values are means of soil cores collected from the four replicates of each treatment. Values within a row followed by a different letter are significantly different ($P < 0.10$). Tukey's Honestly Significant Difference method was used for multi-treatment comparisons.

	Depth (cm)	Treatment [†]							<i>P</i> Value
		C	SP	DB	B/I	B(20)	B(40)	B(80)	
		-----mg kg ⁻¹ -----							
KM	0-5	11.4 ^a	16.6 ^a	23.4 ^a	18.8 ^a	16.6 ^a	22.8 ^a	25.4 ^a	0.2951
P [‡]	5-10	2.8 ^{ab}	2.7 ^b	2.8 ^{ab}	2.9 ^{ab}	2.5 ^b	3.0 ^{ab}	4.9 ^a	0.0273
	10-30	2.1 ^a	1.9 ^a	2.0 ^a	1.9 ^a	2.0 ^a	2.3 ^a	2.3 ^a	0.3667
H ₂ O	0-5	4.9 ^a	7.3 ^a	10.7 ^a	8.1 ^a	7.1 ^a	6.2 ^a	10.2 ^a	0.3072
Sol	5-10	2.1 ^a	1.9 ^a	2.1 ^a	2.6 ^a	1.9 ^a	2.1 ^a	2.7 ^a	0.1873
P [§]	10-30	1.5 ^a	1.5 ^a	1.7 ^a	1.6 ^a	1.6 ^a	1.6 ^a	1.7 ^a	0.5280
		-----µg cm ⁻² -----							
	0-5	0.8 ^a	1.3 ^a	1.9 ^a	1.6 ^a	1.3 ^a	1.6 ^a	1.8 ^a	0.5656
Resin	5-10	0.1 ^a	0.1 ^a	0.2 ^a	0.3 ^a	0.1 ^a	0.2 ^a	0.3 ^a	0.0824
P	10-30	0.1 ^{ab}	0.1 ^{ab}	0.1 ^{ab}	0.0 ^b	0.1 ^{ab}	0.1 ^{ab}	0.1 ^a	0.0326

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

[‡]KM P= Modified Kelowna Extractable P

[§]H₂O Sol P= Water Soluble P

3.5.1.2 Downslope soybean yield

At the Downslope position, soybean grain yield did not differ significantly among any of the treatments ($P=0.12$) when all treatments were analyzed as a single statistical model (Fig. 3.2). When fertilizer application methods were grouped into in-soil (SP, DB, B/I) and surface broadcast alone strategies ((B(20), B(40), and B(80), orthogonal contrasts revealed that in-soil fertilizer application resulted in statistically significantly greater soybean grain yields compared to broadcast (Table 3.5; $P=0.0096$). Further, these contrasts showed that soybean grain yield response differed significantly with in-soil fertilizer application compared to the control, while broadcast application resulted in no difference ($P=0.0488$ and 0.9479 respectively; Table 3.5).

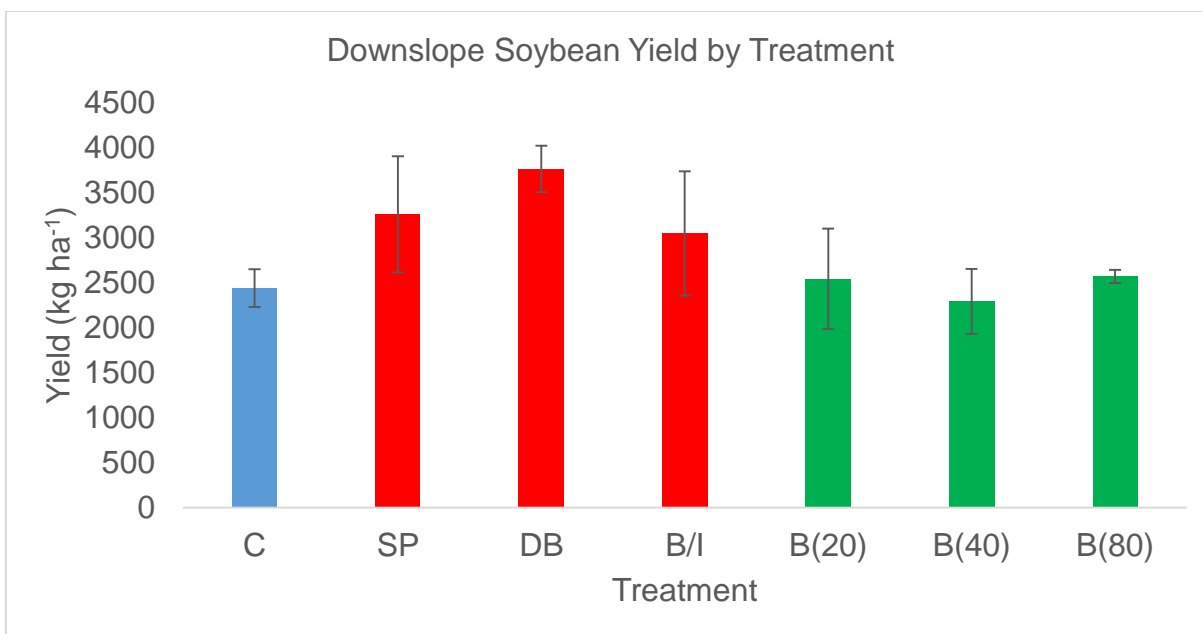


Fig. 3.2. Downslope soybean grain yield by treatment. Reported values are the means of the four replicates of each treatment. Error bars represent the standard error of the four field replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

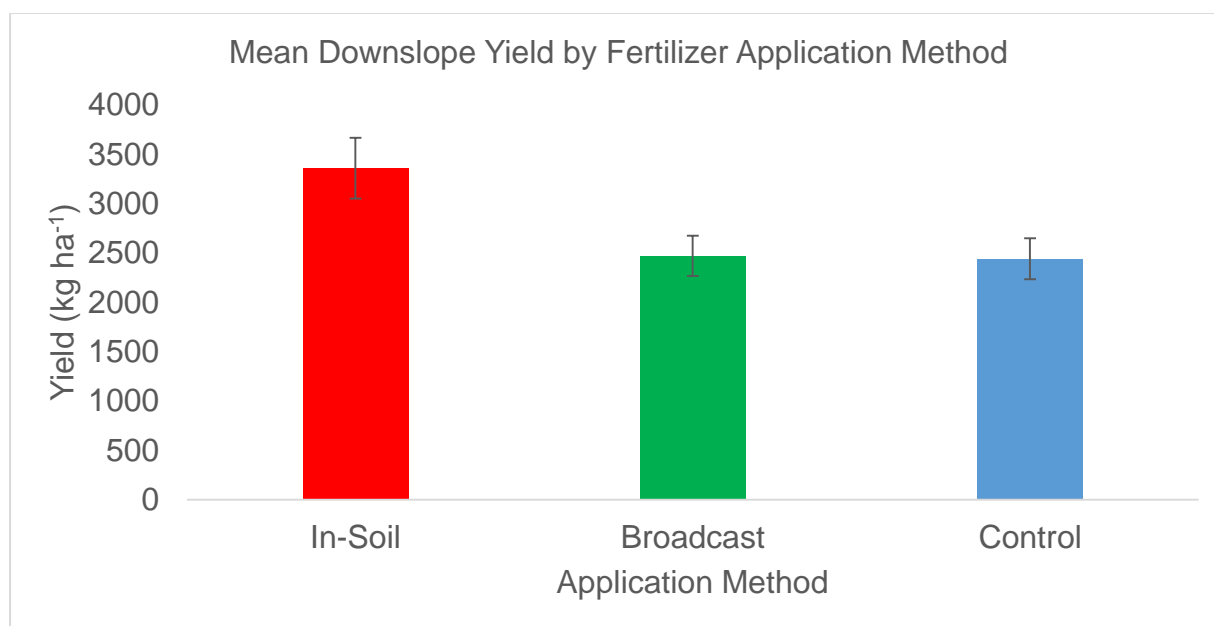


Fig. 3.3. Downslope soybean grain yield by fertilizer application method. Reported values are the means of the three in-soil application methods (SP, DB, and B/I treatments), the three broadcast methods ((B(20), B(40), and B(80) treatments), and the control treatment. There are four replicates of each treatment. Error bars represent the standard error of all the values in each application method. Orthogonal contrasts between the application methods are also provided (Table 3.5). A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P_2O_5 ha⁻¹); DB: Deep band (20 kg P_2O_5 ha⁻¹); B/I: Broadcast with incorporation (20 kg P_2O_5 ha⁻¹); B(20): Broadcast (20 kg P_2O_5 ha⁻¹); B(40): Broadcast (40 kg P_2O_5 ha⁻¹); and B(80): Broadcast (80 kg P_2O_5 ha⁻¹). Red coloured bar collectively denotes in-soil placement of P fertilizer while green coloured bar indicates surface broadcast placement. Blue is the unfertilized control.

Table 3.5 Orthogonal contrasts of soybean grain yield response at the Downslope position between fertilizer application methods.

Orthogonal Contrasts	Treatments [†] Compared	<i>P</i> Value
In-Soil vs. Broadcast	SP, DB, B/I vs. B(20), B(40), B(80)	0.0096
Control vs. In-Soil	C vs. SP, DB, B/I	0.0488
Control vs. Broadcast	C vs. B(20), B(40), B(80)	0.9479

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P_2O_5 ha⁻¹); DB: Deep band (20 kg P_2O_5 ha⁻¹); B/I: Broadcast with incorporation (20 kg P_2O_5 ha⁻¹); B(20): Broadcast (20 kg P_2O_5 ha⁻¹); B(40): Broadcast (40 kg P_2O_5 ha⁻¹); and B(80): Broadcast (80 kg P_2O_5 ha⁻¹).

3.5.1.3 Upslope soybean yield

Soybean grain yield did not differ significantly among treatments in the Upslope position ($P=0.73$; Fig. 3.4). In contrast to the Downslope position, no significant difference in soybean

yield was detected between in-soil and broadcast fertilizer application methods (Fig. 3.5; $P=0.95$). In general, the variability in yield response observed at the Upslope position was even greater than that of the Downslope position. This is likely due to the greater inherent variability in soil physical and chemical characteristics present at the Upslope position, which is situated on an eroded knoll.

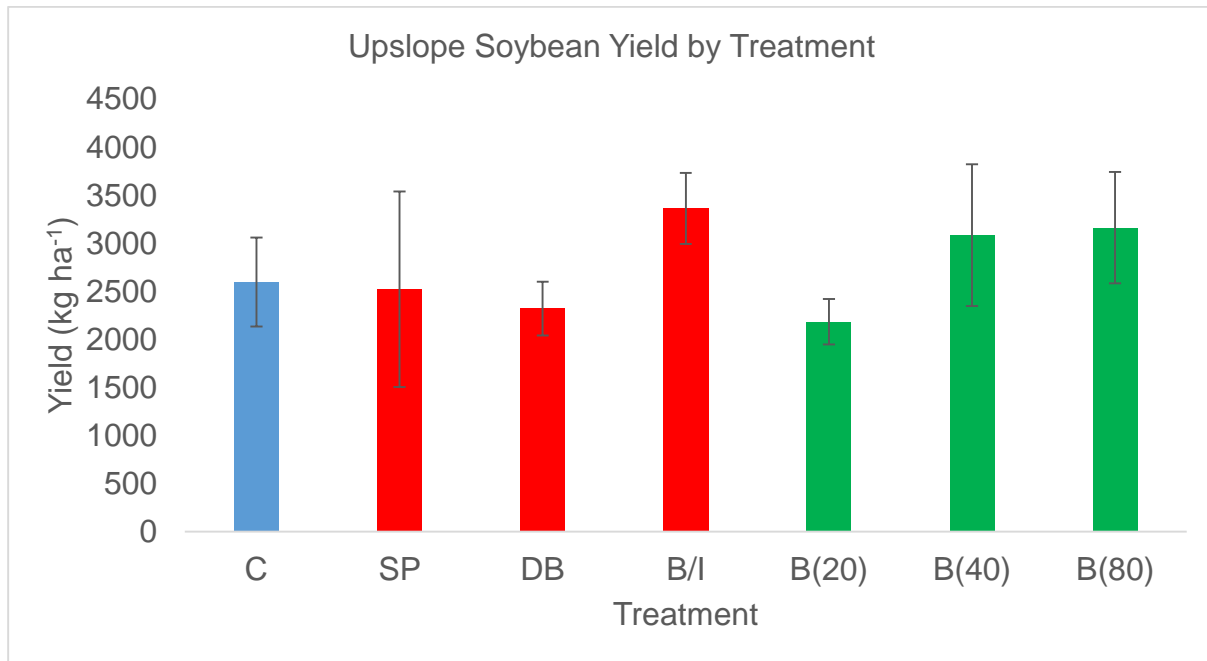


Fig. 3.4. Upslope soybean grain yield by treatment. Reported values are the means of the four replicates of each treatment. Error bars represent the standard error of the four field replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

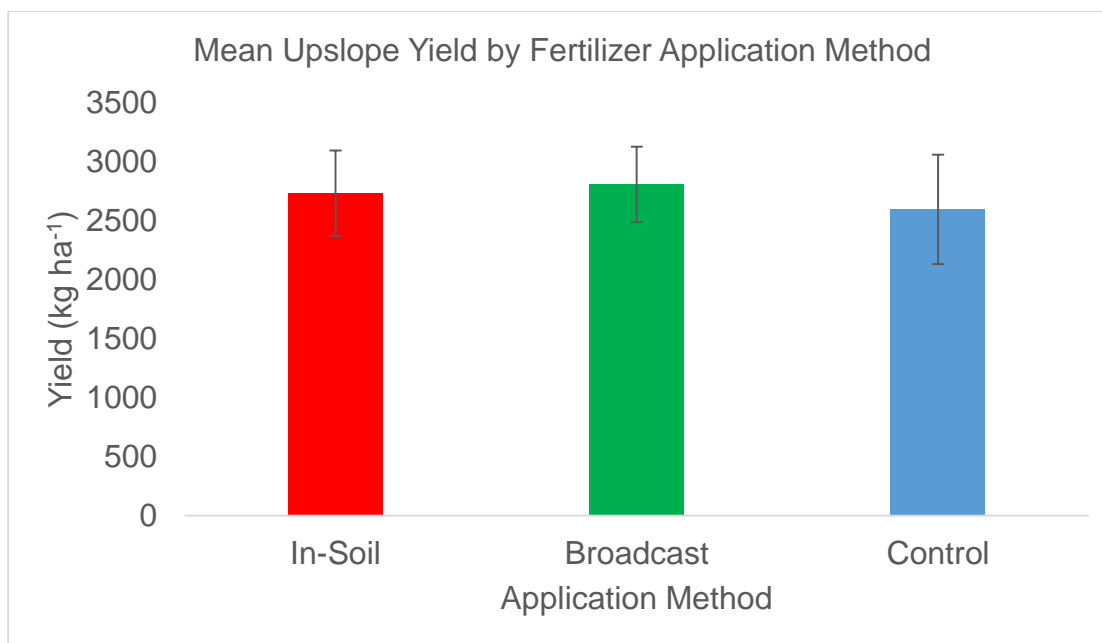


Fig. 3.5. Upslope soybean grain yield by fertilizer application method. Reported values are the means of the three in-soil application methods (SP, DB, and B/I treatments), the three broadcast methods (B(20), B(40), and B(80) treatments), and the control treatment. There are four replicates of each treatment. Error bars represent the standard error of all the values in each application method. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹). Red coloured bar collectively denotes in-soil placement of P fertilizer while green colored bar indicates surface broadcast placement. Blue is the unfertilized control.

3.5.1.4 Plant phosphorus uptake and recovery

Soybean grain and straw yield, P uptake, and recovery of added fertilizer P for the Downslope and Upslope positions is presented in Table 3.6 and Table 3.7, respectively. At the Downslope position (Table 3.6), P uptake in soybean grain was significantly affected by fertilizer application method ($P < 0.10$). Although not statistically different, grain P uptake was higher in DB and SP treatments than other treatments. Straw P uptake was not significantly affected by treatment. Apparent calculated recovery of added fertilizer P in the grain and straw of the soybean was greatest for the deep band treatment (31.0 %), closely followed by the seed-placed treatment (25.0 %), while broadcast treatments were much lower. Fertilizer P application method had a significant effect on P uptake in soybean grain at the Upslope position (Table 3.7) with the higher P uptake in grain occurring in the B(40) and B(80) broadcast treatments. All

other measurements were not significantly influenced by fertilizer P application method ($P>0.10$). At the Upslope position, total P recovery was greatest when fertilizer P was broadcast at 20 kg P₂O₅ ha⁻¹ followed by an incorporation event. High variability in yield at this Upslope site and lack of significant effects limits the ability to make inferences based on percent recovery calculations at this site.

Table 3.6 Mean soybean grain and straw yield, grain, straw, and total P uptake and % recovery of added P fertilizer in grain and straw measured in fall 2014 at the Downslope position. Reported values are the means of the four replicates of each treatment. Means (n=4) within a row followed by different letters are significantly different (Tukey's HSD, $P<0.05$).

Parameter	Treatment [†]							P Value
	C	SP	DB	B/I	B(20)	B(40)	B(80)	
Grain Yield (kg ha ⁻¹)	2442 ^a	3262 ^a	3768 ^a	3050 ^a	2545 ^a	2295 ^a	2571 ^a	0.12
Straw Yield (kg ha ⁻¹)	5189 ^a	6189 ^a	6323 ^a	5021 ^a	4556 ^a	4295 ^a	4510 ^a	0.29
Grain P Uptake (kg ha ⁻¹)	11.3 ^a	16.4 ^a	17.7 ^a	12.5 ^a	11.6 ^a	11.0 ^a	13.1 ^a	0.08
Straw P Uptake (kg ha ⁻¹)	3.4 ^a	4.3 ^a	4.2 ^a	3.6 ^a	4.3 ^a	5.1 ^a	4.8 ^a	0.77
Plant P Recovery [‡] (%)	-	25.0	31.0	1.5	1.0	-0.3	2.3	-

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

[‡]kg ha⁻¹ above-ground plant P in fertilized minus kg ha⁻¹ above-ground plant P in control divided by kg ha⁻¹ fertilizer P added, multiplied by 100.

Table 3.7 Mean soybean grain and straw yield, grain, straw, and total P uptake and P recovery measured in fall 2014 from the Upslope position. Reported values are the means of the four replicates of each treatment. Means (n=4) within a row followed by different letters are significantly different (Tukey's HSD, $P<0.05$).

Parameter	Treatment [†]							<i>P</i> Value
	C	SP	DB	B/I	B(20)	B(40)	B(80)	
Grain Yield (kg ha ⁻¹)	2598 ^a	2521 ^a	2321 ^a	3362 ^a	2185 ^a	3084 ^a	3163 ^a	0.73
Straw Yield (kg ha ⁻¹)	4373 ^a	4040 ^a	4350 ^a	5729 ^a	4206 ^a	4697 ^a	5048 ^a	0.66
Grain P Uptake (kg ha ⁻¹)	10.6 ^{bc}	6.8 ^c	10.2 ^{bc}	14.9 ^{ab}	8.7 ^c	17.1 ^a	16.4 ^{ab}	<0.01
Straw P Uptake (kg ha ⁻¹)	3.2 ^a	2.9 ^a	3.7 ^a	5.2 ^a	2.8 ^a	3.8 ^a	3.1 ^a	0.12
Plant P Recovery [‡] (%)	-	2.0	0.5	30.5	-5.5	9.0	5.9	-

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

[‡] kg ha⁻¹ above-ground plant P in fertilized minus kg ha⁻¹ above-ground plant P in control divided by kg ha⁻¹ fertilizer P added, multiplied by 100.

3.5.2 Controlled environment study

3.5.2.1 Soybean seedling emergence and biomass production

Rate of seed-placed fertilizer P had a significant effect ($P<0.0001$) on soybean emergence measured 14 days after planting (Fig. 3.6). Mean soybean emergence was highest with the control and 20 kg P₂O₅ ha⁻¹ rate of fertilizer P application which were not significantly different from one another. Additionally, multi-treatment comparisons revealed that mean soybean emergence was significantly greater in the control treatment compared to mean emergence with the three highest rates of fertilizer P application (40, 60, and 80 kg P₂O₅ ha⁻¹). Seed placed fertilizer P application rate also significantly influenced mean soybean biomass production measured 14 days after seeding ($P=0.002$). Mean soybean biomass was significantly lower when

fertilizer P was applied at the highest rate (80 kg P₂O₅ ha⁻¹) compared to the control treatment, or the 20 kg P₂O₅ ha⁻¹ application rate (Fig. 3.7).

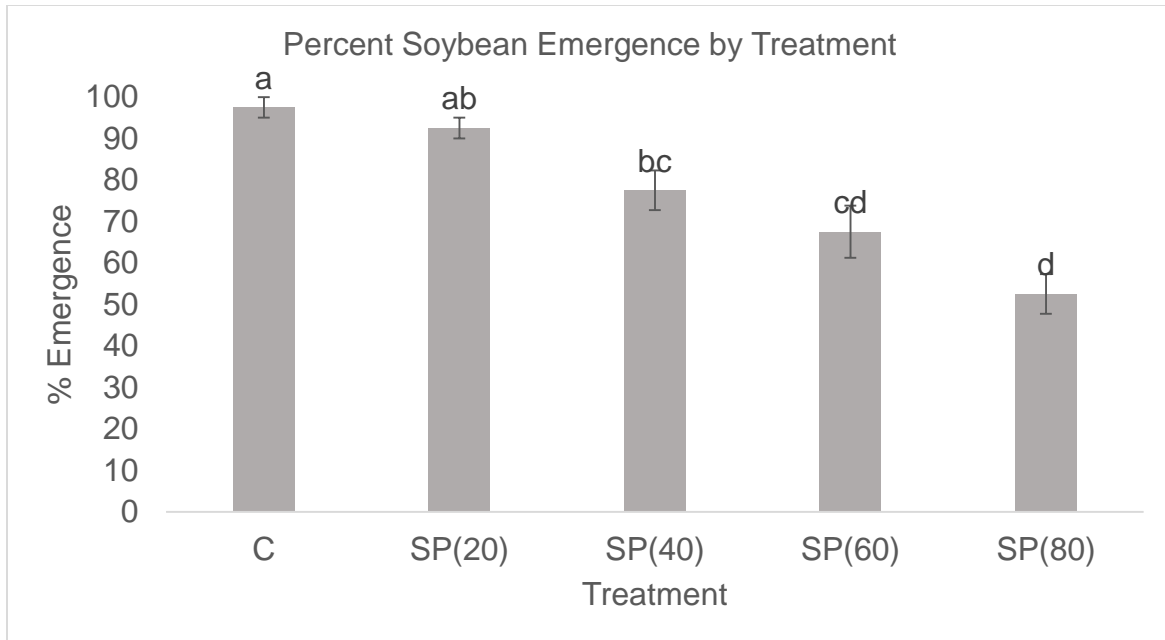


Fig. 3.6. Soybean emergence (percentage of planted seeds that emerged above ground) measured 14 days after seeding as a function of varying rates of seed placed fertilizer P. Reported values are the means of the four replicates of each treatment. Error bars represent the standard error of the four replicates of each treatment. Means (n=4) with different letters are significantly different (Tukey's HSD, $P < 0.05$). A description of the treatments is as follows: C: Control (no P); SP(20): Seed-placed (20 kg P₂O₅ ha⁻¹); SP(40): Seed-placed (40 kg P₂O₅ ha⁻¹); SP(60): Seed-placed (60 kg P₂O₅ ha⁻¹); and SP(80): Seed-placed (80 kg P₂O₅ ha⁻¹).

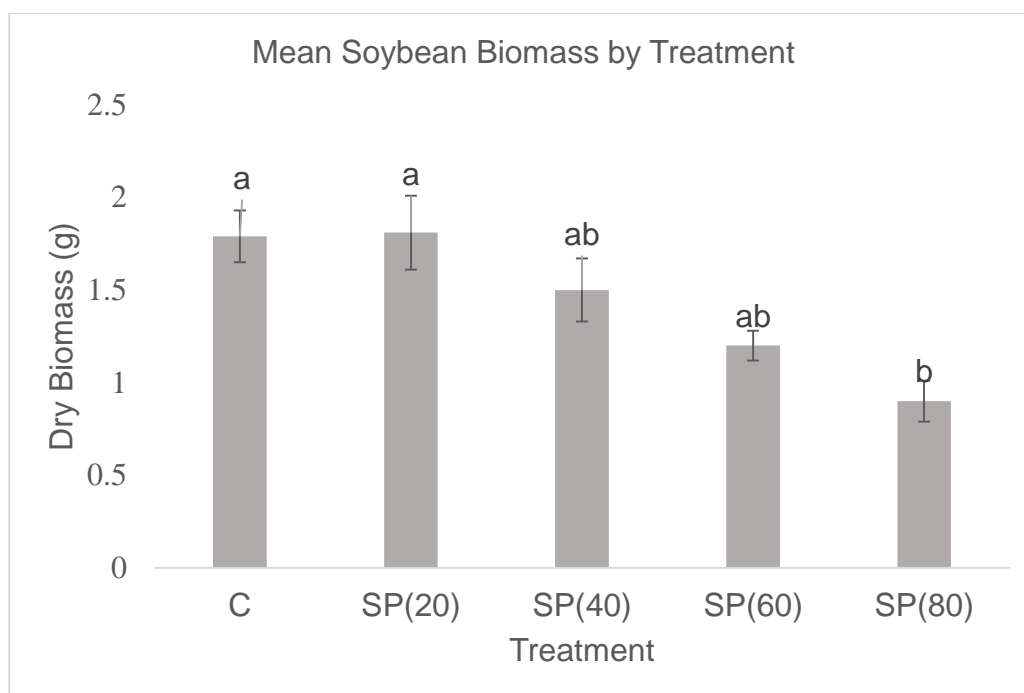


Fig. 3.7. Soybean above-ground dry matter biomass with different rates of seed placed fertilizer P measured 14 days after seeding. Error bars represent the standard error of the four replicates of each treatment. Means ($n=4$) with different letters are significantly different (Tukey's HSD, $P<0.05$). A description of the treatments is as follows: C: Control (no P); SP(20): Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); SP(40): Seed-placed ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); SP(60): Seed-placed ($60 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and SP(80): Seed-placed ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$).

3.5.2.2 Faba bean emergence and biomass production

In contrast to soybean, mean faba bean emergence measured 14 days after seeding was not significantly different among seed-placed P_2O_5 treatments ($P=0.24$; Fig. 3.8) and percent emergence was above 80%, even at the $80 \text{ kg seed placed P}_2\text{O}_5 \text{ ha}^{-1}$ rate. However, mean faba bean biomass production two weeks after seeding was found to be significantly affected by seed placed fertilizer P application rate ($P=0.01$). A significant decrease in mean biomass production was observed when fertilizer P was applied at the two highest rates (i.e. 60 and $80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$) compared to the control treatment. Mean faba bean biomass production did not differ significantly between the control treatment and when fertilizer P was applied at a rate of 20 or $40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ (Fig. 3.9).

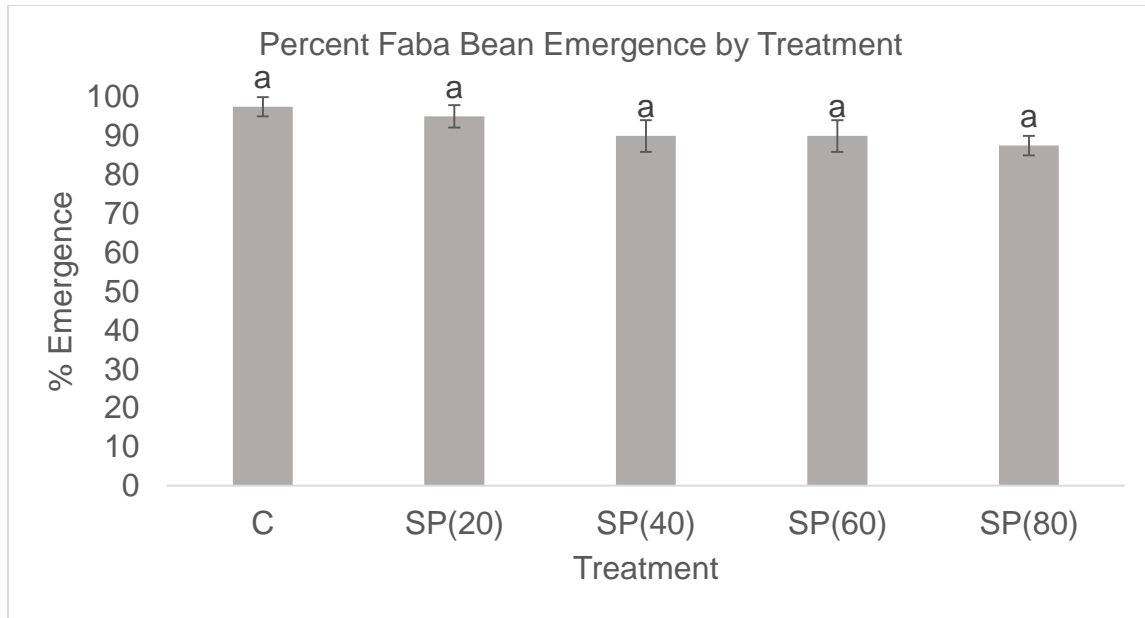


Fig. 3.8. Faba bean emergence (percentage of planted seeds that emerged above ground) measured 14 days after seeding as a function of varying rates of seed placed fertilizer P. Error bars represent the standard error of the four replicates of each treatment. A description of the treatments is as follows: C: Control (no P); SP(20): Seed-placed (20 kg P_2O_5 ha⁻¹); SP(40): Seed-placed (40 kg P_2O_5 ha⁻¹); SP(60): Seed-placed (60 kg P_2O_5 ha⁻¹); and SP(80): Seed-placed (80 kg P_2O_5 ha⁻¹).

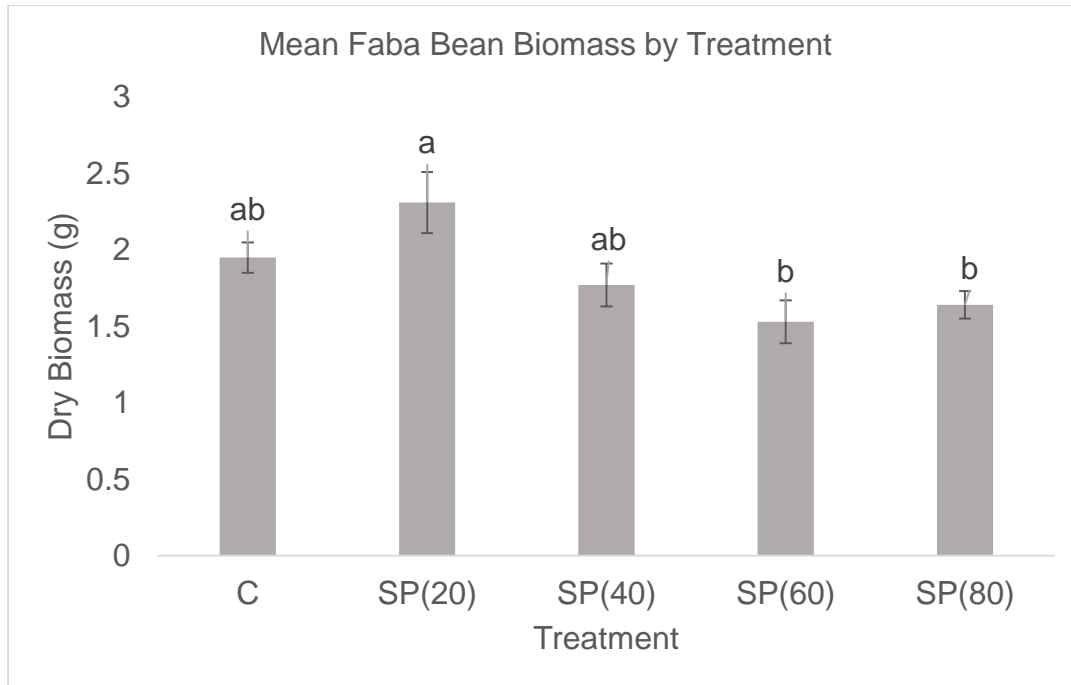


Fig. 3.9. Faba bean above-ground dry matter biomass with different rates of seed placed fertilizer P measured 14 days after seeding. Error bars represent the standard error of the four replicates of each treatment. Means (n=4) with different letters are significantly different (Tukey's HSD, $P < 0.05$). A description of the treatments is as follows: C: Control (no P); SP(20): Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); SP(40): Seed-placed ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); SP(60): Seed-placed ($60 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and SP(80): Seed-placed ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$).

3.6 DISCUSSION

3.6.1 Field study

3.6.1.1 Soil nutrients

Each of the three STP extractions utilized in this chapter (KM extractable P, water soluble P, and anion exchange resin P) were carefully chosen based on their relevance to the objectives of this thesis. Modified Kelowna extractable P and anion exchange resin P are both believed to assess plant available P in soil (Qian et al., 1994; Qian and Schoenau, 2002) and consequently may be related to soil P mobility and its environmental fate in snowmelt run-off water. An assessment of water soluble P was particularly important in this study, as Sharpley et al. (2008) noted that water soluble P concentration may be more closely related to the P released from soil during a run-off event than other extraction procedures. Further, the readily dissolvable orthophosphate that is removed from soil by water may be easily taken up by aquatic organisms and is known to promote eutrophication (Sharpley and Smith, 1993; Sharpley et al., 1994; Sharpley et al., 1996). Soil test P concentrations were increased at the soil surface (0 to 5 cm depth) when fertilizer P was applied at 40 and 80 kg P₂O₅ ha⁻¹ in the broadcast treatments. Other researchers have reported enrichment in STP levels in surface soil layers from broadcast fertilizer application compared to in-soil placement (Borges and Mallarino, 2000; Borges and Mallarino, 2003; Farmaha et al., 2012). The higher concentration of STP at the soil surface in broadcast treatments predicts greater export of phosphorus off-site in snowmelt run-off water from soils receiving these treatments, which is examined in detail in Chapter 4.

3.6.1.2 Soybean yield

At the Downslope site, the greatest soybean grain yield response to fertilizer P application at the 20 kg P₂O₅ ha⁻¹ rate was observed when it was placed in a deep band below the seed, followed closely by seed-row placement. Broadcast treatments had yields that were similar to the control, even when rates were 40 and 80 kg P₂O₅ ha⁻¹. This finding is in agreement with

current recommendations on the Canadian prairies, which state that, when possible, fertilizer P should be applied in a band at, or in close proximity to, the seed row (Grant, 2012). This is also supported by Robinson (1996), who noted that application of fertilizer P in a band induced root proliferation at the depth of band placement and resulted in better crop access to water and other nutrients. Hairston et al. (1990) also observed an increased soybean yield response to banded P application compared to broadcast application in a study in Mississippi, USA.

Soybean yield did not show a statistically significant response ($P=0.72$) to P fertilization in the Upslope position, regardless of fertilizer application method. Further, no significant difference was observed at the Upslope position even when treatments were grouped into those in which fertilizer P was in-soil applied and those where it was broadcast. Although a yield response would have been expected based on the STP results obtained from initial site characterization, the large degree of variability among treatments may be a reflection of inherent variability in soil physical and chemical properties at the Upslope position and may have led to the lack of detectable yield response. For example, factors such as the direction of tillage and slope gradient may have a profound influence on the total amount of topsoil displaced by tillage, resulting in variable exposure of calcareous subsoil across the knoll (Lobb, 2011).

Initial site characterization revealed that the study site was considered marginally deficient to deficient in plant available P according to the KM extraction method (See Fig. A1, Appendix A and ALS Labs interpretation). A yield response to fertilizer P was predicted and expected and was observed in the Downslope site. The soil test P is therefore considered a good predictor of the response of short season soybean to added P. As the KM soil test extracts about 50% of the P extracted by the Bray method (Qian et al., 1994), the observation of a response of soybean yield to added P at a KM-P level of less than 10 mg P kg⁻¹ in this study is in agreement with Borges and Mallarino (2003) who found a response when Bray-P level was less than 19 mg P kg⁻¹.

The results of this study confirm our hypothesis that in-soil fertilizer application is more efficient than broadcast application in terms of promoting yield (Fig. 3.3). Interestingly broadcast fertilizer P was not able to produce the same yield response as banded fertilizer application, even when it was applied at a fourfold rate, as in treatment B(80). Kostuik et al. (2013) in a study conducted in Manitoba, Canada also noted this lack of soybean yield response when fertilizer P

was broadcast at a rate of 80 kg P₂O₅ ha⁻¹ compared to when it was applied with the seed at 20 kg P₂O₅ ha⁻¹.

Therefore, one may conclude that P placed in the soil in a band below or with the seed is superior to broadcast application to overcome P deficiency and increase short season soybean yield on the Canadian prairies. Apart from the effects that fertilizer placement strategy may have on crop yield, Borges and Mallarino (2000) observed significant soil P stratification, with enrichment near the soil surface, from broadcast fertilizer P application as is noted in the current study. For this reason, soil P distribution in the soil profile was examined in detail in this thesis work and is covered in Chapter 4.

3.6.1.3 Plant phosphorus uptake and recovery

At the Downslope position, soybean grain P uptake was significantly influenced by fertilizer P application method ($P=0.08$). Phosphorus uptake in soybean grain was greatest when fertilizer P was applied in a deep band below the seed, with seed-placed application only slightly lower. Additionally, recovery of applied P was much greater for the SP and DB treatments (25% and 31%, respectively) compared to all other treatments (Table 3.7). Water soluble P levels measured in the surface soil layer (i.e. 0 to 5 cm) after crop harvest were significantly lower when fertilizer P was seed-placed or applied in a deep band compared to when it was broadcast. This suggests that the use of fertilizer P application methods such as placement with the seed or in a band below the seed leads to greater P uptake by the crop, will reduce soil P enrichment in surface soil layers compared to broadcast fertilizer P application, and contribute to reduced P run-off potential. This is in agreement with other researchers who have suggested in-soil fertilizer P application methods as effective strategies to reduce enrichment of surface soil layers in STP, with the potential to also reduce the off-site transport of P in agricultural run-off water (Farmaha et al., 2012).

3.6.2 Controlled environment study

3.6.2.1 Soybean emergence and biomass production

Placement of fertilizer P in the seed row at a rate of 20 kg P₂O₅ ha⁻¹ did not cause a significant reduction in soybean emergence, while seed-placed application at higher rates (40,

60, and 80 kg P₂O₅ ha⁻¹) negatively affected emergence. Soybean is known to be sensitive to high rates of MAP applied in the seed row under low seed-bed utilization (wide rows and narrow openers), with reductions in seedling emergence caused primarily from osmotic effects (Grant, 2012). The results of this study are in agreement with results of recently conducted field-scale trials in Manitoba, Canada, where seed-placed application of MAP at a rate of 80 lb P₂O₅ ac⁻¹ caused a significant reduction in soybean plant density compared to the control treatment at certain sites (Kostuik et al., 2013). The authors in this study observed that soil texture was a controlling factor on mitigating the toxic effects of seed-placed fertilizer P, as coarse-textured soils were more affected by damage potential than fine-textured soils (Kostuik et al., 2013). Therefore, as the soil used in this study has a clay loam texture, a significant reduction in soybean emergence when fertilizer P was applied at the 60 and 80 kg P₂O₅ ha⁻¹ rates seems reasonable.

Rate of seed-placed fertilizer P application had a significant effect on soybean biomass production measured 14 days after seeding ($P=0.002$). However, only the 80 kg P₂O₅ ha⁻¹ application rate resulted in significantly lower biomass production compared to the control treatment. Kostuik et al. (2013) observed a significant reduction in soybean biomass in plants grown to physiological maturity at only one site out of five when fertilizer P was applied at 80 kg P₂O₅ ha⁻¹. Importantly, however, the same rate of fertilizer P application resulted in a significant reduction in soybean seed yield at three sites out of five, with the effect more pronounced at sites having a coarse soil texture (Kostuik et al., 2013). It should also be noted that no positive yield response to increasing rates of seed-placed fertilizer P was observed. The soil used in this thesis research had a KM extractable P concentration of 32 mg P kg soil⁻¹, which is greater than the threshold STP level where a positive yield response to fertilizer P application is anticipated (see section 3.6.1.2). Furthermore, soybean roots are reported to have good ability to scavenge surface soil layers for water and nutrients (Barber, 1995). Therefore, soybean may have been able to access sufficient soil P under the limited rooting volume of the containers used in this study, consequently negating any positive yield response.

Current recommendations for soybean production state that fertilizer P should not be applied in the seed row at rates in excess of 20 kg P₂O₅ ha⁻¹ (Risula et al., 2015b). The results of this study show that seed-placed application of fertilizer P at 40 kg P₂O₅ ha⁻¹ did not cause a significant reduction in biomass production. This is further supported by the work of Kostuik et

al. (2013), who did not observe a significant difference in soybean biomass production or seed yield when fertilizer P was applied at a rate of 40 kg P₂O₅ ha⁻¹. Grant (2012) reported that application of seed-placed fertilizer P at only 20 kg P₂O₅ ha⁻¹ for soybean production has the potential to cause significant soil P depletion as amounts removed in crop harvest are much greater than this. Therefore, it may be justified to increase the currently recommended rate of seed-placed fertilizer P upward from 20 to perhaps 30 or 40 kg P₂O₅ ha⁻¹ for soybean production. This may help to mitigate soil P depletion in crop rotations containing soybean and other high P users on the Canadian prairies.

3.6.2.2 Faba bean emergence and biomass production

Rate of seed-placed fertilizer P application ranging from 0 to 80 kg P₂O₅ ha⁻¹ did not have a significant effect on faba bean seedling emergence ($P=0.24$). However, application rate of seed-placed fertilizer P did have a significant effect on faba bean biomass production ($P=0.01$). Application of MAP at rates in excess of 40 kg P₂O₅ ha⁻¹ resulted in significantly lower faba bean biomass production two weeks after seeding compared to the unfertilized treatment, or when fertilizer P was applied at 20 or 40 kg P₂O₅ ha⁻¹. The results of this study support the current recommended safe rates of seed-placed fertilizer P for faba bean production in Saskatchewan (Government of Saskatchewan, 2012) of 40 kg P₂O₅ ha⁻¹. A review of the literature has revealed a lack of studies on the Canadian prairies regarding the yield response of faba bean to varying rates of fertilizer P. This lack of research interest may be a reflection of the fact that although commercial faba bean production in western Canada began in 1972, interest among producers in growing the crop has fluctuated since its introduction (McVicar et al., 2015). It should be noted that faba bean was planted on only 10,000 ac in Saskatchewan in 2013, a minor fraction of the total arable land in Saskatchewan (Arnason, 2014).

4. EFFECT OF FERTILIZER APPLICATION METHOD AND RATE ON THE OFF-SITE TRANSPORT OF PHOSPHORUS IN WATER

4.1 Preface

The objective of the work described in this chapter was to assess the effect that fertilizer P application method has on the environmental fate of P including P species in the surface of the soil interacting with run-off water, and the export of P from soil and crop residue in snowmelt run-off water. Chapter 3 covered the effects of P placement and rate on crop uptake and soil P in the 2014 growing season. This chapter examines in detail the potential fate of P left behind at the surface at the end of the growing season after harvest. Spectroscopic methods, including XANES spectroscopy and a sequential chemical extraction, were employed to assess forms of P in surface soil samples collected from the treatment plots. A simulated runoff experiment was conducted in which snow was placed on top of soil slabs removed from the Upslope position plots in the field trial after harvest in 2014 and allowed to melt under controlled environmental conditions. Snowmelt water was analyzed for soluble and particulate P. Additionally, a simulated freeze-thaw cycle experiment was conducted to assess the amount of soluble P released from soybean residue that was harvested from each plot.

4.2 Abstract

The aim of this study was to assess the effect that fertilizer P application method has on residual soil P distribution, speciation of fertilizer P reaction products in soil, and the potential off-site transport of P in snowmelt run-off water. Intact soil monoliths were removed after soybean harvest from plots fertilized with 20 kg P₂O₅ ha⁻¹ granular mono-ammonium phosphate that was seed-placed, deep banded, broadcast and incorporated, or broadcast alone in the spring in the Upslope position of a cultivated Brown Chernozem located near Central Butte, Saskatchewan. A microscale assessment of residual soil P distribution revealed that broadcast application of fertilizer P resulted in significant enrichment in modified Kelowna extractable P in the surface (5 cm depth) soil layer. Spectroscopic investigations using P XANES revealed that, from a qualitative perspective, fertilizer application method influenced speciation of fertilizer P reaction products. The sequential chemical extraction revealed that broadcast fertilizer P application resulted in greater concentrations of organic P forms compared to the control treatment or fertilizer P application in a band below the seed row, suggesting greater fertilizer P immobilization from this application method. Fertilizer application method was found to have a significant ($P=0.03$) effect on P export in simulated snowmelt runoff water from the monoliths. In general, broadcast fertilizer P application resulted in greater P export than the control treatment or when fertilizer P was applied in the soil as a band or broadcast and incorporated. A simulated freeze-thaw cycle experiment was conducted to assess the contribution that the soybean residue makes to total dissolved P in run-off water. A strongly significant correlation was found between total P contained in the soybean straw and content of dissolved phosphate in the water from the freeze-thaw cycle experiment in both Downslope and Upslope positions ($P<0.001$; $r=0.73$ and $P<0.001$; $r=0.78$, respectively).

4.3 Introduction

Special consideration must be given to potential P losses from agricultural soils on the prairies in the early spring season of the Canadian prairies. For Lake Winnipeg, it is estimated that 45% of the run-off load that enters the lake from its watershed takes place from April to July, predominantly in the form of snowmelt run-off water and spring rain (Lake Winnipeg Stewardship Board, 2006). The overall goal of the research work described in this chapter was to assess the effect that fertilizer application method has on off-site transport of P in snowmelt run-

off water. Fertilizer application method has been shown to have a significant effect on influencing the soil P distribution in the soil profile and crop uptake and removal of P after a season of crop growth, as discussed in Chapter 3. The findings in Chapter 3 are supported by the work of many others (e.g. Borges and Mallarino, 2003), who have noted that broadcast fertilizer P application results in lower crop P use efficiency and significant enrichment in soil P near the surface compared to in-soil application, mainly as a result of the low mobility stranding the P at the surface. This has important implications for the environmental fate of P in run-off water. (McIsaac et al., 1995; Borges and Mallarino, 2000; Borges and Mallarino, 2003; Farmaha et al., 2012). Additionally, Khatiwada et al. (2012) found that fertilizer P application method influences speciation of soil P, and suggested that deep banded fertilizer P may have both agronomic and environmental benefits compared to broadcast application. It was hypothesized, therefore, that as banded fertilizer P results in increased crop P uptake and a reduction in soil P stratification compared to broadcast P application, this fertilizer application method will result in reduced off-site transport of P in run-off water. Further, as fertilizer P banded resulted in increased P uptake by soybean compared to broadcast fertilizer P application, this fertilizer P application method is anticipated to result in a greater amount of TDP to be released from soybean residue compared to the broadcast application after a simulated freeze-thaw cycle.

4.4 MATERIALS AND METHODS

4.4.1 Soil phosphorus characterization

4.4.1.1 Soil monolith sampling method for detailed soil P characterization

Nailboards were used to extract intact rectangular soil samples from one plot of each treatment (Fig. 4.1) on the Upslope position of the site described in Chapter 3 to assess impact of placement on residual distribution of P in the soil after harvest. Samples were collected from one block of replicate treatments according to a previously established technique described by Kar et al. (2012). Briefly, nailboards measuring approximately 20 cm by 30 cm were constructed from 1.25 cm thick plywood, with 7.6 cm nails driven through the plywood on a 5 cm by 5 cm grid. A trench approximately 20 cm depth by 30 cm length and 10 cm width was excavated within the plot to be sampled and the wall of the trench was smoothed to allow for a uniform depth of soil to be removed. The nailboard was inserted into the side of the trench, centred on the middle seed row of the plot, and the location of the seed row was marked on the nailboard. Nailboards were

then removed with the intact soil sample by excavating around the trench wall. Upon removal, the nailboards were wrapped in plastic and stored at 5°C until subsampling took place. A grid was established in which transects were centered on the seed row and a sample was taken using a stainless steel micro-coring device of 0.79 cm diameter at the seed row, and extending away from the seed-row in both horizontal directions from the origin providing a total of five samples per horizontal transect (Fig. 4.2). Vertical transects extended downward, with samples collected at 1 cm, 4 cm, 7 cm, and 10 cm depths from the soil surface. The collected sub-samples were air dried, ground to pass a 2 mm sieve, and stored at room temperature for wet chemical extraction and spectroscopic analysis using XANES as described below.



Fig. 4.1. Photo showing nailboard used for removing soil monoliths from selected plots of the Upslope position.



Fig. 4.2. Photo showing subsamples taken from a soil monolith along four horizontal transects at varying depths from the soil surface.

4.4.1.2 Residual soil phosphorus distribution

Phosphorus depletion in the soybean rooting zone was mapped by determining extractable P concentrations at each of the subsample transect points taken from the soil nailboard monoliths using the KM extraction procedure (Qian et al., 1994; Ashworth and Mrazek, 1995). Briefly, 30 mL of Modified Kelowna solution (acetic acid, ammonium acetate, and ammonium fluoride) was added to 3 g of air-dried soil. Samples were then shaken horizontally on a rotary shaker for 5 min at 142 RPM. After shaking, samples were filtered through VWR 454 filter paper, and the filtrate was stored at 5°C until analysis by AA-FE spectrometry. For presentation purposes, values were reported as normalized to the values measured at each subsampling location in the control treatment (Fig. 4.7 to Fig. 4.12).

4.4.1.3 Soil phosphorus speciation

Phosphorus XANES spectroscopy

Sample selection

Subsamples were obtained from the soil cores taken from the soil nailboard monoliths to assess residual soil P distribution. These samples were chosen to represent four fertilizer P

application methods: 1) broadcast without incorporation, 2) fertilizer P banded below the seed row, 3) fertilizer P placed in the seed-row, all at rates of $20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$, and 4) a control treatment which received no fertilizer P. Further details on application can be found in section 3.4.1.4 of Chapter 3. To maximize signal to noise ratio in the data, sample points in the vertical-horizontal grid of the monolith grids were chosen to assess soil P speciation at the point of maximum P enrichment, as determined by the results of the Modified Kelowna method, as described above. This resulted in soil P speciation being determined on samples collected at the soil surface (i.e. 1 cm deep) and at the seed row for the control, seed placed, and broadcast without incorporation treatments, and on a sample collected at a 4 cm depth and at the seed row for the deep banded treatment.

Sample preparation

After samples were selected, a small amount of each sample (less than 1 mg) was ground to a fine powder with a mortar and pestle. One side of a piece of double sided carbon tape (measuring approximately 1 cm by 1 cm) was stuck to a copper plate and small subsample of each soil was carefully adhered to the other side of the double-sided tape. A spatula was used to ensure that an even layer of soil was spread across the entire surface of the tape. Once all samples were prepared, the copper plate was placed in the sample chamber of the experimental hutch at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source (CLS).

4.4.1.4 Sequential chemical extraction

A sequential chemical extraction procedure as outlined by Tiessen and Moir (2008) was used to characterize various soil P pools on twenty samples collected from the soil monoliths as outlined in section 4.4.1.1. From each monolith, a subsample was taken from the seed row at the depth of maximum enrichment. Additionally, a subsample was taken from a 10 cm horizontal distance from the seed row at the depth of maximum enrichment. This procedure involves the completion of several extraction steps over a five day period, and is outlined in Fig. 4.3 below.

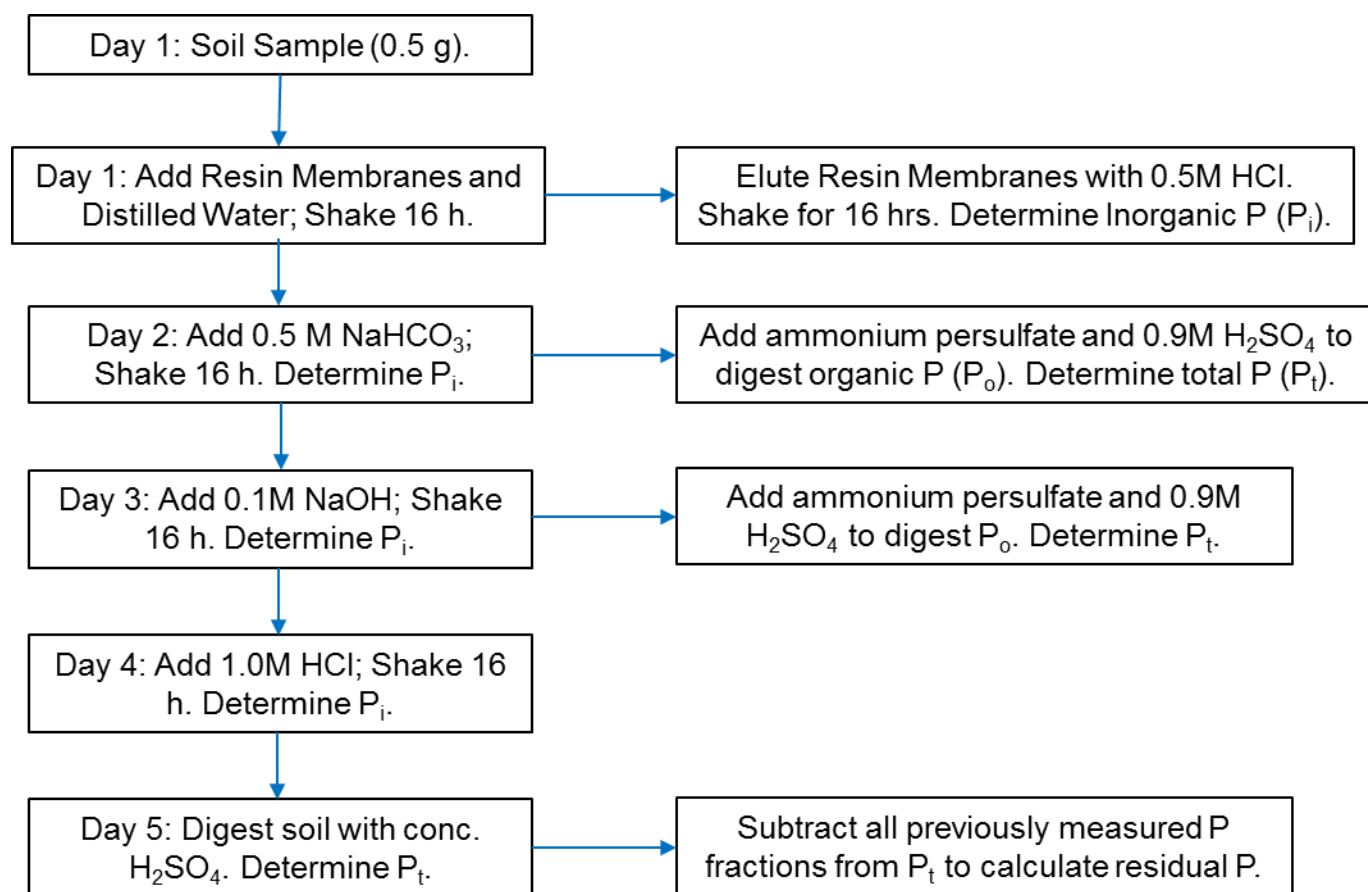


Fig. 4.3. Schematic of sequential P extraction procedure, as outlined by Tiessen and Moir (2008).

4.4.2 Simulated runoff experiment

4.4.2.1 Sample collection

In tact soil slabs were obtained from each plot of all treatments on the Upslope position of the site described in Chapter 3 in preparation for the simulated runoff experiment. The Upslope position was used for the run-off study as this site is convex in topography, and consequently would represent the origin of run-off events in the field. Further, the destructive nature of the sampling technique limited the number of plots to which the technique was applied. In this method, an in tact slab of soil (25 cm by 20 cm by 15 cm) was removed from each plot by excavating a 15 cm deep trench on all four sides of the slab to be extracted. A hand-held saw was then used to cut the exposed sample, and the sample was lifted intact onto a PlexiglasTM

((Poly(methyl methacrylate)) sheet (Fig. 4.4). The extracted soil slab was refrigerated (5°C) until laboratory analysis.



Fig. 4.4. Photo of an in-tact soil slab removed from a plot of the Upslope position.

4.4.2.2 Experimental apparatus

The simulated run-off experiment was conducted according to King and Schoenau (2009). A schematic depicting the apparatus used in the simulated run-off experiment is shown in Fig. 4.5 below. Briefly, the soil slabs were placed at a 5° angle in a plastic-lined, insulated box (Fig. 4.6). One kg of snow (equating to approximately 8 cm of snow depth on a per area basis) was placed on top of the soil slab and allowed to melt at room temperature (~17.5°C). After 24 h, one additional kilogram of snow was placed on top of the soil slab and melted at room temperature. The second addition of snow was necessary to ensure that an adequate amount of snowmelt water was able to be collected. Run-off and leachate water was allowed to run into a plastic sample collection pail and after agitation, a subsample of the water was collected in a plastic storage bottle. Water samples were frozen at -20°C until preparation for analysis.

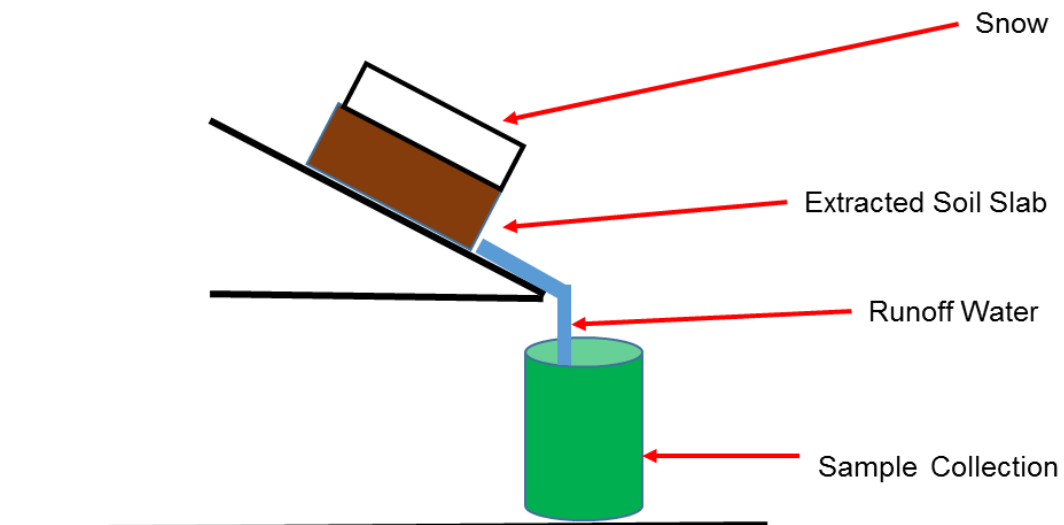


Fig. 4.5. Schematic of simulated runoff experiment.



Fig. 4.6. Photo of apparatus used for simulated runoff experiment.

Collected run-off and leachate water was filtered through a 0.45 μm Millipore™ filter and filtered samples were placed in a freezer at -20°C until analyses. The suspended material removed from the water during the filtration process, representing the particulate P fraction, was also collected and an acid digest of collected particulate P was performed to assess total P concentration in this fraction. Plant Root Simulator (PRS™) probes were also placed on the soil

surface prior to the addition of snow to assess exchangeable P at the soil-run-off water interface (Qian and Schoenau, 2002).

4.4.2.3 Exchangeable phosphorus at soil-runoff water interface

Plant Root Simulator Probes were used to assess exchangeable P supply rate at the soil-run-off water interface. These probes were prepared to assess anion exchange rate according to the method of Qian et al. (2008), and as described in detail in Chapter 3. Prior to the addition of snow in the simulated run-off experiment, probes were inserted horizontally into the top of soil slab at a depth (2 cm) to ensure adequate soil-probe contact. Snow was then added, as described in section 4.4.2.2 and allowed to melt at room temperature. Probes were then removed from the soil and promptly washed with distilled water to remove any remaining soil adhering to the probe. Then, probes were then placed in a plastic bag and 20 mL of 0.5M HCl was added. Care was taken to ensure that air was removed from the bag to ensure complete contact between the probe and HCl eluent. After 1 h, probes were removed from the plastic bag and the remaining eluent was stored in a refrigerator until analysis by Technicon automated colorimetry.

4.4.2.4 Snow water equivalent calculation

Snow water equivalent was calculated according to King and Schoenau (2009). A known quantity of snow (450 g), collected from the Goodale Research Farm near Saskatoon, Canada, was allowed to melt at room temperature. This snow was collected from the same area as the snow that was used for the simulated run-off experiment (section 4.4.2.2). Upon melting, water was collected in a plastic vial and its mass was determined. Additionally, TDP in the water was measured to establish a background P concentration in the snowmelt water. Snow water equivalent was calculated according to equation three below. This revealed that the collected snow was approximately 97% water.

$$\text{Snow water equivalent (\%)} = \frac{\text{mass of water (g)}}{\text{mass of snow (g)}} \times 100 \quad [3]$$

4.4.2.5 Laboratory analyses

Total dissolved phosphorus (TDP) export

Water samples collected from the simulated run-off experiment were vacuum filtered through a 0.45 μ m membrane filter. After filtration, samples were frozen until analysis for TDP by automated Technicon automated colorimetry.

Total phosphorus digest of particulate fraction

An acid digest was conducted on particulate P collected after run-off water samples had been filtered through a 0.45 μ m filter, as described in Section 4.4.2.2. This digest was performed according to previously established methods (Tiessen and Moir, 2008). Briefly, a known quantity of material was weighed into glass digestion tubes and 5 mL of conc. H₂SO₄ was added. Samples were then placed on a digestion block at 360°C for 30 min. Following this, samples were removed from the digestion block, allowed to cool, and 0.5 mL H₂O₂ was added. Samples were then placed on the digestion block an additional seven times for 30 min, adding H₂O₂ after each heating period. Finally, samples were placed on the digestion block for 1 h. After samples were allowed to cool, distilled water was added to dilute the final volume of the sample to 25 mL to achieve a final concentration above the detection limit and within the operating range (linear portion of the standard curve) of the analyzing instrument. Samples were placed in a refrigerator at 4°C until analysis by Technicon automated colorimetry.

4.4.3 Freeze-thaw cycle experiment

4.4.3.1 Experimental set up

To assess the contribution that soybean straw residue makes to the off-site transport of P in run-off water, a water soluble P extraction of the crop residue was conducted according to the method employed by Liu et al. (2014). From each plot, after-harvest crop residue samples were collected from an area representing 0.25 m². From this sample, a subsample of 25% of the collected residue from each plot was placed into polyethylene bags and 1.875 L of deionized water was added to each bag. This amount of water is used to represent 3 cm of run-off per cm² of crop area. After sealing the bags with plastic zip-ties, taking care to ensure that air was

excluded from the system, the bags were shaken by hand for 30 s to ensure complete residue-water contact. The bags were then stored at room temperature for 24 h, followed by exposure to -20°C for 24 h outside to simulate freezing field conditions so the residue and water were completely frozen.

4.4.3.2 Water soluble phosphorus extraction of soybean residue

The extraction procedure included bringing frozen samples inside and allowing them to thaw for 16 h at room temperature. After thawing, a plastic colander was placed over a plastic bucket, and the contents of each bag were poured into the colander. After allowing the samples to drain by gravity for 1 min and the contents of the bucket to settle for 5 min, a sample of the water extract (approximately 500 mL) was collected in a plastic storage bottle for analyses.

4.4.3.3 Laboratory analyses

Phosphorus release from soybean residue

Leachate water collected as described in Section 4.4.2.2, was vacuum filtered through a 0.45µm membrane filter. Water samples were then frozen until analysis for TDP and Total Dissolved Nitrogen (TDN) by AA-FE spectrometry.

Acid digest of leached soybean residue

An acid digest of soybean residue following the freeze-thaw cycle experiment was conducted according to the method of Thomas et al. (1967) and as described for the particulate fraction in section 4.4.2.5.

4.4.4 Data analysis

Phosphorus XANES data were analyzed using Athena XAS Data Processing software (Ravel and Newville, 2005). Spectra of three replicates of each sample were collected at the SXRMB beamline of the CLS. Data from each spectra was normalized to the P k-edge peak (~2153 eV). The three replicates were aligned to one another and merged into a single spectrum. This was done to increase the signal-to-noise ratio of the collected data, thereby improving

resolution in elucidating P speciation. A single repetition of a three-point smoothing algorithm was used to further reduce noise in the data. Where necessary, certain data points were removed from each data set, where x-ray diffraction caused unnecessary signal to be detected.

4.4.5 Statistical analyses

Statistical analyses were conducted using PROC MIXED of SAS, Version 9.3 (SAS Institute Inc, 2012). The study to determine P export from soybean residue was conducted as a RCBD with a total of seven treatments in replicates of four. An ANOVA was conducted, with treatments as a fixed effect and block as a random effect. PROC UNIVARIATE was used to determine if the residual and block data were normally distributed. Where applicable, multi-treatment comparisons were conducted using the Tukey Test, and employing the HSD method. All tests were declared significant at the 10% level. PROC CORR was used to determine the relationship between soybean P uptake and P release from soybean residue following a simulated freeze-thaw cycle.

4.5 RESULTS

4.5.1 Soil phosphorus characterization

4.5.1.1 Residual soil phosphorus distribution

Soil P distribution was influenced by fertilizer application strategy, with significant P enrichment found at the point of fertilizer application. For the broadcast ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$) treatment, P enrichment was evident from the soil surface to an approximate depth of 4 cm (Fig. 4.7). When fertilizer P was broadcast and incorporated (Fig. 4.8), soil P enrichment extended to the depth of incorporation (approximately 7 cm). The seed placed fertilizer P application (Fig. 4.9) resulted in significant soil P enrichment at the seed row from the soil surface to an approximate depth of 4 cm. Banded fertilizer application directly below the seed (Fig. 4.10) caused significant soil P enrichment in the seed row zone, but slightly deeper in the soil profile than the seed placed treatment (7 cm). When fertilizer P was broadcast at a rate of $40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ (Fig. 4.11), significant soil P enrichment from the soil surface to a depth of approximately 4 cm was evident, as with the broadcast application of fertilizer P at $20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$, but the magnitude of the enrichment was far greater. Finally, broadcast application of fertilizer P at a

rate of 80 kg P₂O₅ ha⁻¹ (Fig. 4.12) resulted in a residual soil P distribution that was unexpected. Fifty percent of the subsample locations from this treatment showed soil P enrichment relative to the control treatment, while 50% of the subsample locations revealed depletion or no change in soil P relative to the control treatment. The high variability in this treatment may be associated with variability in soil or uneven distribution of the P fertilizer across the plot sampled. Nailboard sampling of more than one block of treatment replicates would have been desirable to provide a more representative depiction of treatment effects.

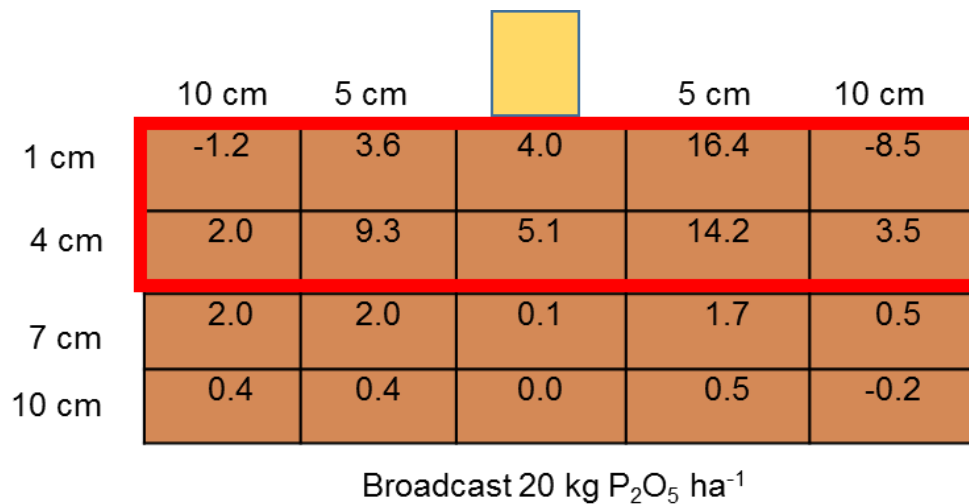


Fig. 4.7. Soil P distribution in the soil profile after 1 season of crop growth for treatment 5 (broadcast P at 20 kg P₂O₅ ha⁻¹). The yellow box indicates the position of the seed row. Values are reported as mg P kg soil⁻¹ extracted by the Modified Kelowna method and are normalized to the values measured at each subsampling location in the control treatment.

	10 cm	5 cm		5 cm	10 cm
1 cm	1.1	2.8	2.2	-0.4	No Sample
4 cm	0.0	2.4	4.3	2.7	8.0
7 cm	0.6	1.4	2.3	4.4	8.5
10 cm	0.5	0.9	0.4	0.6	0.0

Broadcast with Incorporation

Fig. 4.8. Soil P distribution in the soil profile after 1 season of crop growth for Treatment 4 (broadcast P with incorporation at 20 kg P₂O₅ ha⁻¹). The yellow box indicates the position of the seed-row. Values are reported as mg P kg soil⁻¹ extracted by the Modified Kelowna method and are normalized to the values measured at each subsampling location in the control treatment.

	10 cm	5 cm		5 cm	10 cm
1 cm	-8.1	-4.3	10.9	1.6	-7.8
4 cm	-2.3	0.6	8.7	5.1	1.0
7 cm	0.2	0.6	0.4	1.6	0.5
10 cm	-0.3	0.3	0.9	1.3	0.2

Seed Placed

Fig. 4.9. Soil P distribution in the soil profile after 1 season of crop growth for Treatment 2 (seed-placed P at 20 kg P₂O₅ ha⁻¹). The yellow box indicates the position of the seed-row. Values are reported as mg P kg soil⁻¹ extracted by the Modified Kelowna method and are normalized to the values measured at each subsampling location in the control treatment.

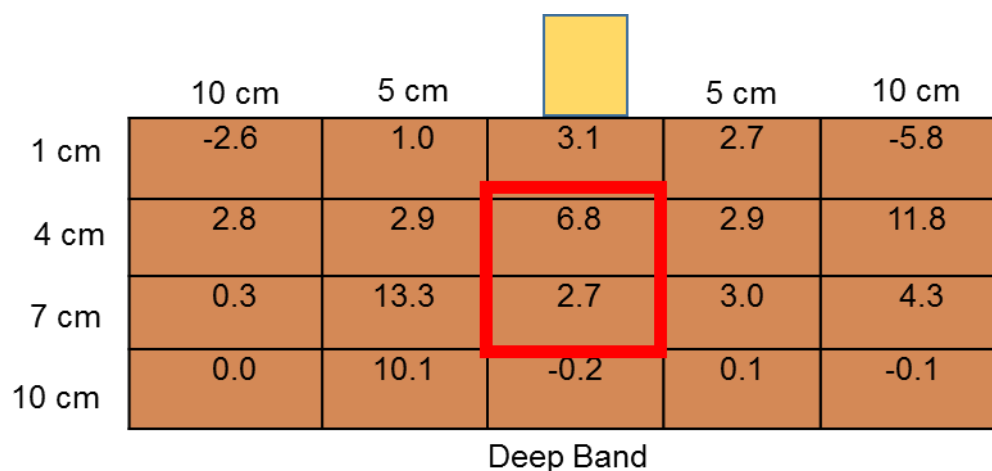


Fig. 4.10. Soil P distribution in the soil profile after 1 season of crop growth for Treatment 3 (P deep banded below seed-row at 20 kg P₂O₅ ha⁻¹). The yellow box indicates the position of the seed-row. Values are reported as mg P kg soil⁻¹ extracted by the Modified Kelowna method and are normalized to the values measured at each subsampling location in the control treatment.

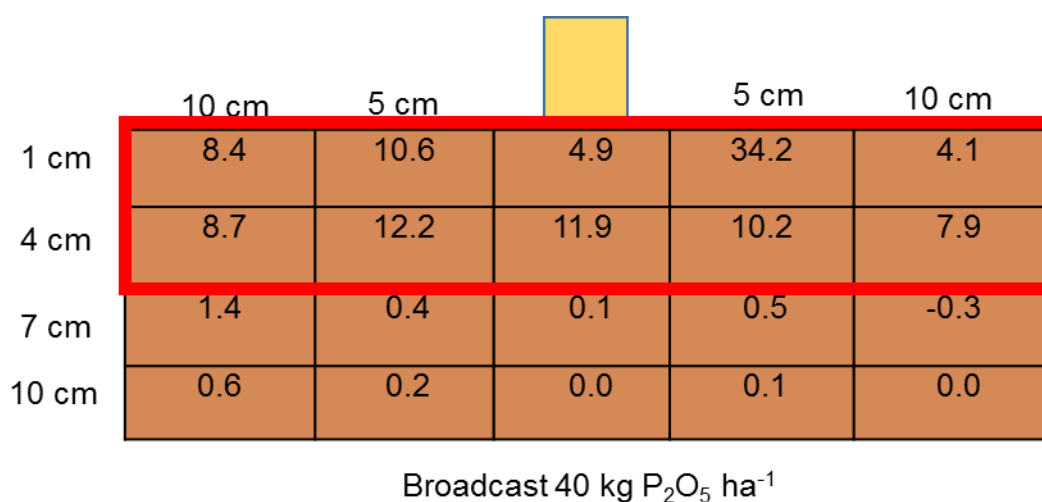


Fig. 4.11. Soil P distribution in the soil profile after 1 season of crop growth for Treatment 6 (broadcast at 40 kg P₂O₅ ha⁻¹). The yellow box indicates the position of the seed-row. Values are reported as mg P kg soil⁻¹ extracted by the Modified Kelowna method and are normalized to the values measured at each subsampling location in the control treatment.

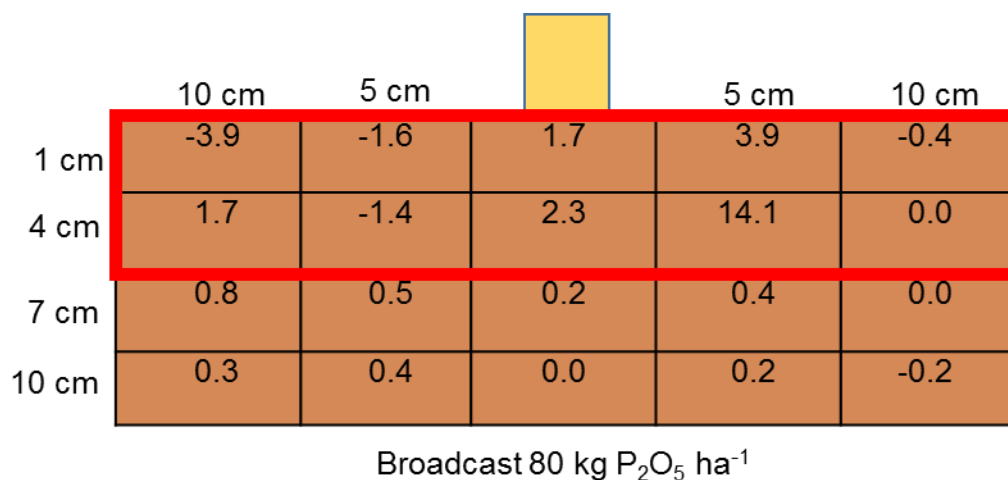


Fig. 4.12. Soil P distribution in the soil profile after 1 season of crop growth for Treatment 7 (broadcast at 80 kg P₂O₅ ha⁻¹). The yellow box indicates the position of the seed-row. Values are reported as mg P kg soil⁻¹ extracted by the Modified Kelowna method and are normalized to the values measured at each subsampling location in the control treatment.

4.5.1.2 Soil phosphorus speciation

Phosphorus XANES spectroscopy

The P k-edge white line peak was measured at 2153 eV (Fig. 4.13). A distinct pre-edge feature characteristic of Fe-PO₄ minerals such as strengite and adsorbed Fe-PO₄ species was observed for the control and broadcast followed by incorporation treatments. Further, a characteristic post-edge shoulder, commonly observed in Ca-PO₄ minerals was observed for the control treatment.

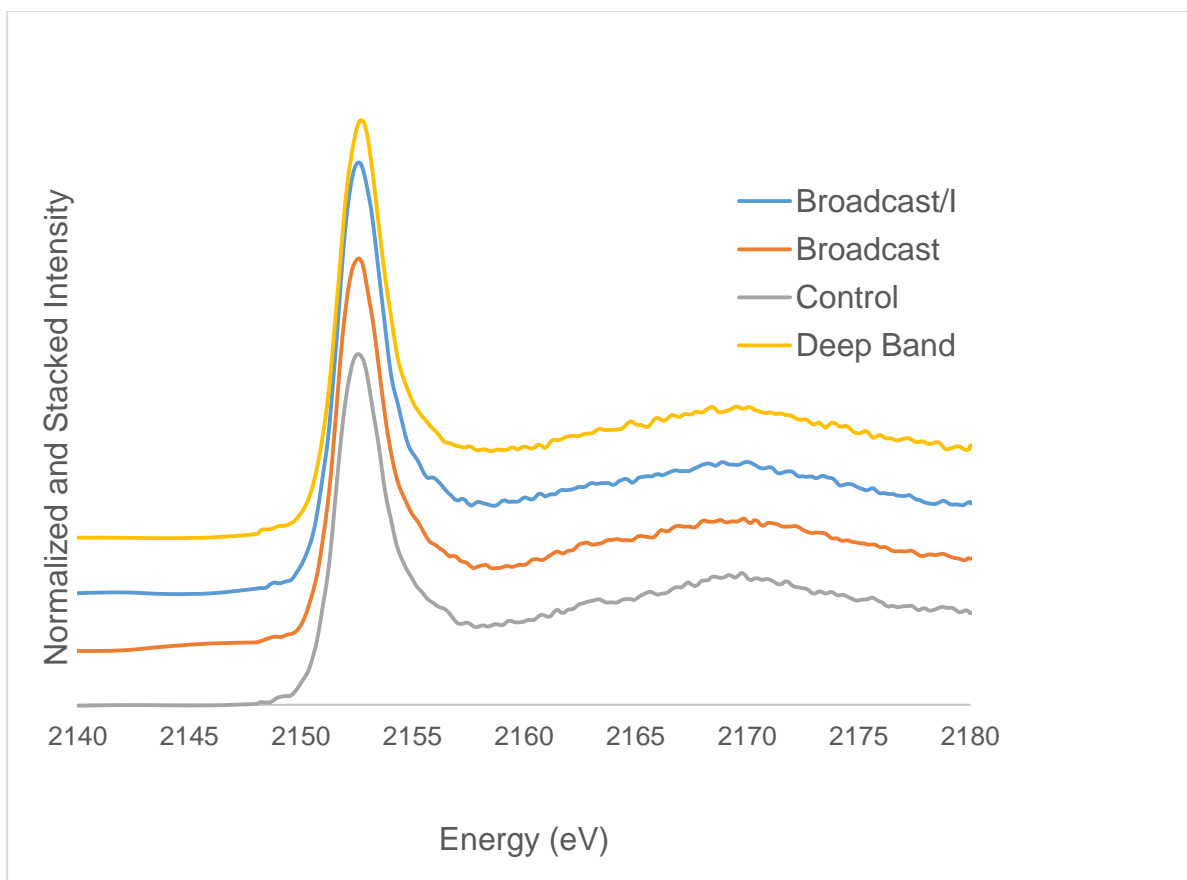


Fig. 4.13. Phosphorus XANES spectra collected from selected treatments of the field study described in Chapter 3.

4.5.1.3 Sequential chemical extraction

The complete results of the sequential chemical extraction of all soil samples are contained in Appendix A. Soil P pools measured in selected treatments are presented in Fig 4.14 to Fig 4.17 below. In general, P_o pools extracted with 0.5M NaHCO_3 , 0.1M NaOH , and 1.0M HCl , as well as resin extractable P were larger when fertilizer P was broadcast and incorporated compared to the control treatment or when it was applied in a band below the seed row. Interestingly, application of banded fertilizer P resulted in measured P concentrations in the various pools similar to when no fertilizer P was applied. This may reflect the P being concentrated deeper in the soil in the banded treatment (see Fig. 4.10), thus too far away to influence P species close to the soil surface.

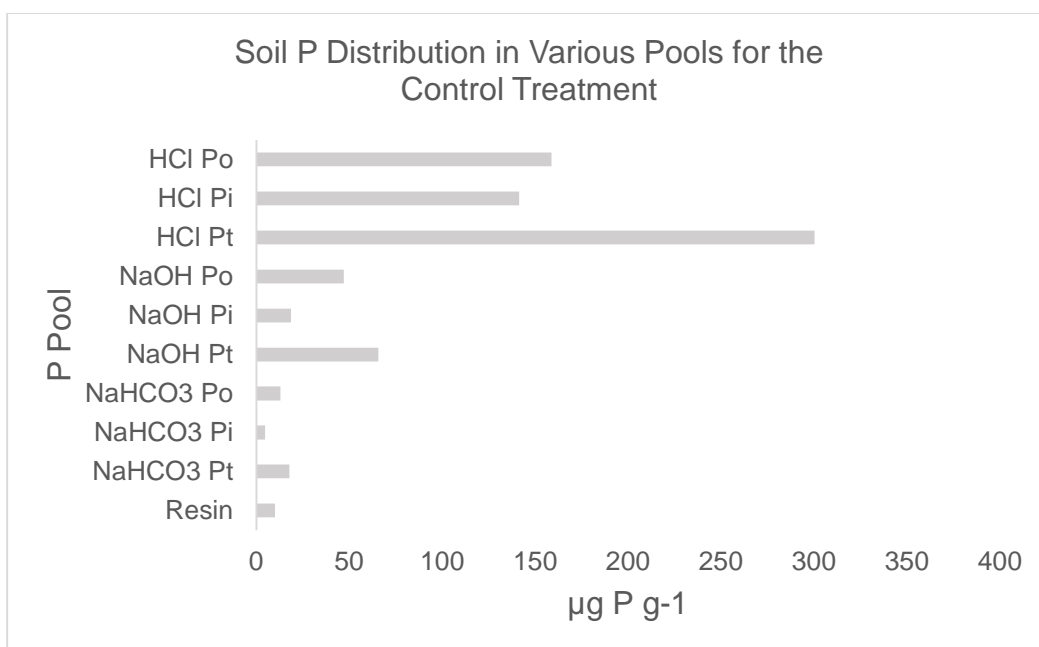


Fig. 4.14. Soil P pools in the surface (0 to 5 cm) soil as determined by sequential chemical extraction in the control treatment. P_i , P_o , and P_t denote inorganic, organic, and total P respectively.

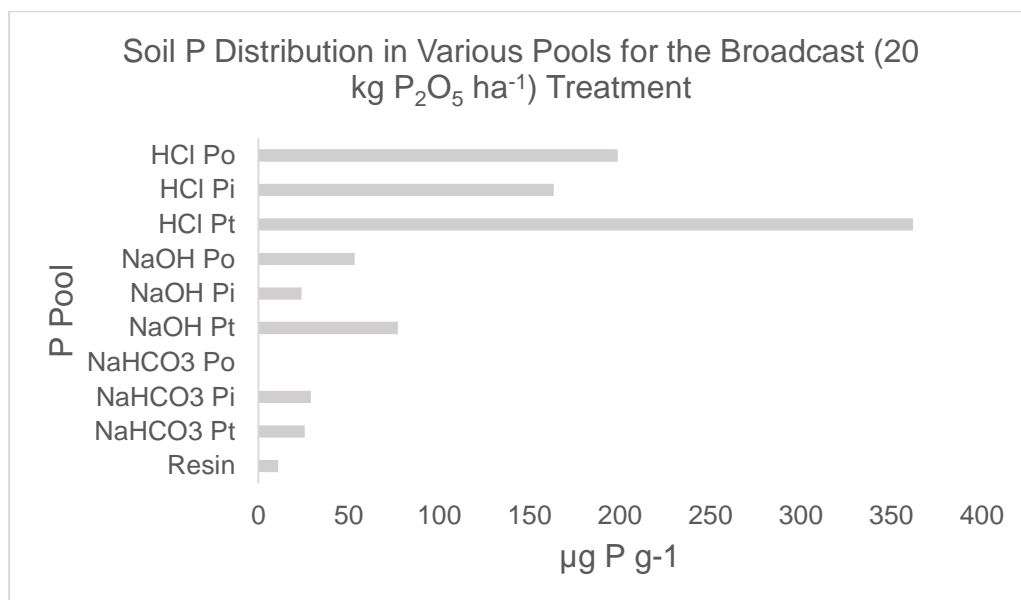


Fig. 4.15. Soil P pools in the surface (0 to 5 cm) soil as determined by sequential chemical extraction in the Broadcast (20 kg P₂O₅ ha⁻¹) treatment. P_i , P_o , and P_t denote inorganic, organic, and total P respectively.

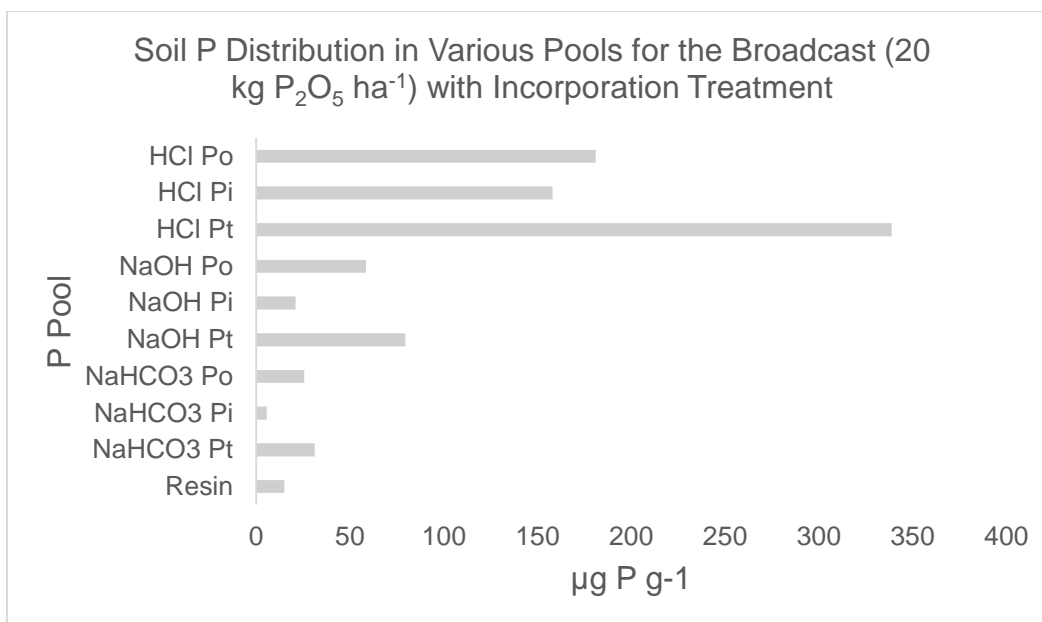


Fig. 4.16. Soil P pools in the surface (0 to 5 cm) soil as determined by sequential chemical extraction in the Broadcast and Incorporation treatment. P_i, P_o, and P_t denote inorganic, organic, and total P respectively.

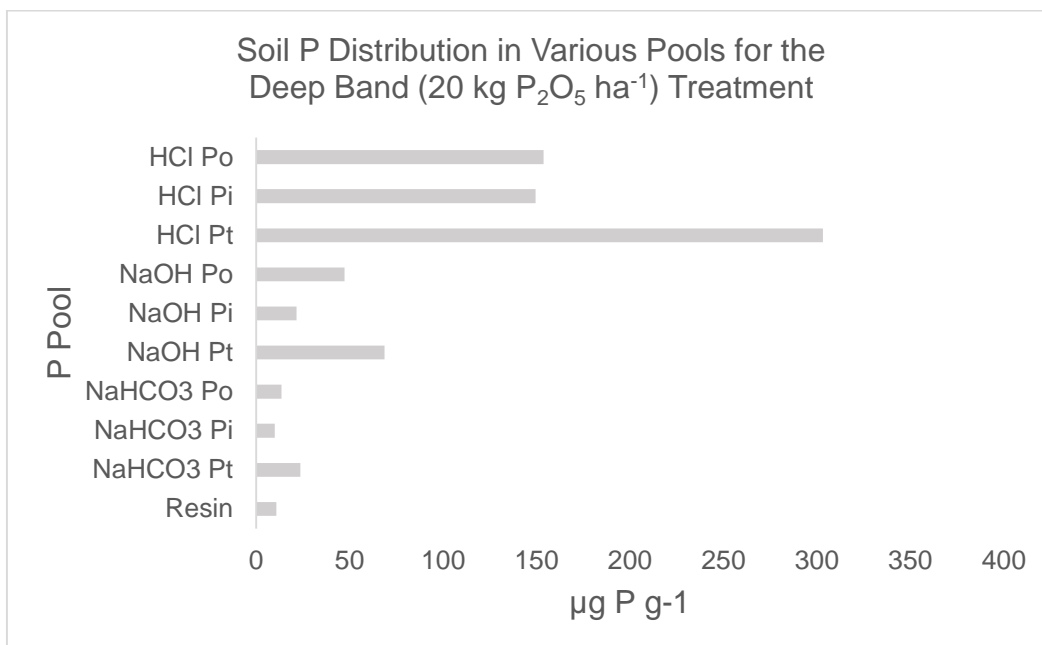


Fig. 4.17. Soil P pools in the surface (0 to 5 cm) soil as determined by sequential chemical extraction in the Deep Band treatment. P_i, P_o, and P_t denote inorganic, organic, and total P respectively.

4.5.2 Simulated run-off experiment

4.5.2.1 Total dissolved phosphorus export

Fertilizer P application method and rate was found to have a statistically significant effect on TDP export ($P=0.03$). Broadcast application of fertilizer P at 20 kg P_2O_5 ha^{-1} resulted in greater TDP export compared to the control treatment or when fertilizer P was applied into the soil (incorporated, seed-placed, deep banded) (Fig. 4.18).

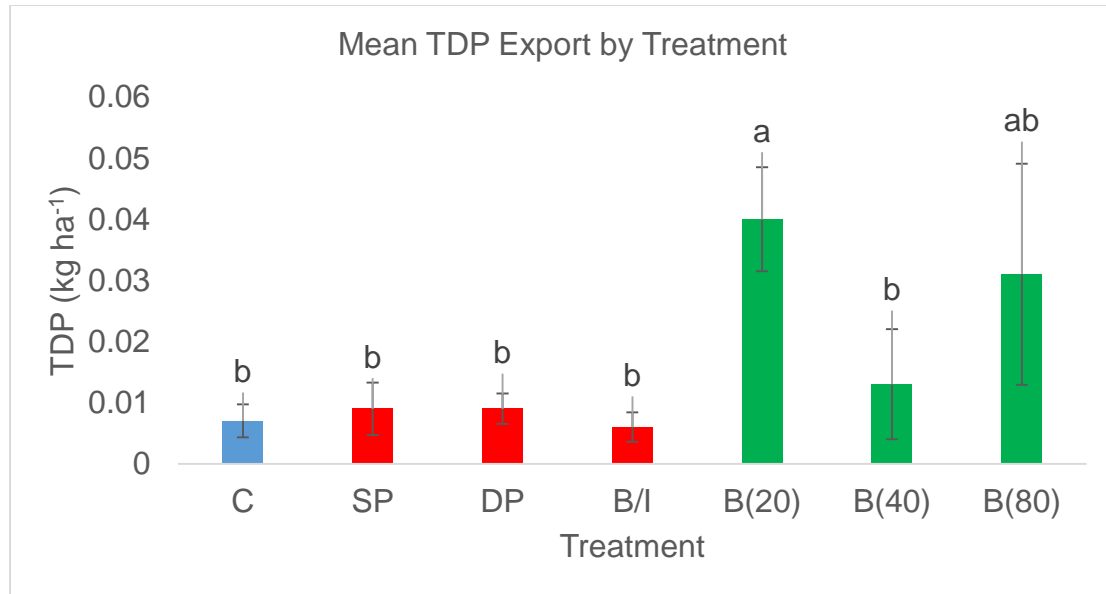


Fig. 4.18. Mean Total Dissolved Phosphorus (TDP) export as a function of fertilizer P application method and rate following a simulated snowmelt runoff experiment. Error bars represent the standard error of the four replicates of each treatment. Means ($n=4$) with different letters are significantly different (Tukey's HSD, $P<0.05$). A description of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P_2O_5 ha^{-1}); DP: Deep band (20 kg P_2O_5 ha^{-1}); B/I: Broadcast with incorporation (20 kg P_2O_5 ha^{-1}); B(20): Broadcast (20 kg P_2O_5 ha^{-1}); B(40): Broadcast (40 kg P_2O_5 ha^{-1}); and B(80): Broadcast (80 kg P_2O_5 ha^{-1}). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

4.5.2.2 Exchangeable phosphorus at soil-run-off water interface

Plant Root Simulator probes were placed on the soil surface during the simulated run-off experiment to assess exchangeable P at the soil-run-off water interface. Fertilizer P application method did not significantly influence exchangeable P measured at the soil-run-off water interface ($P=0.40$) (Fig. 4.19).

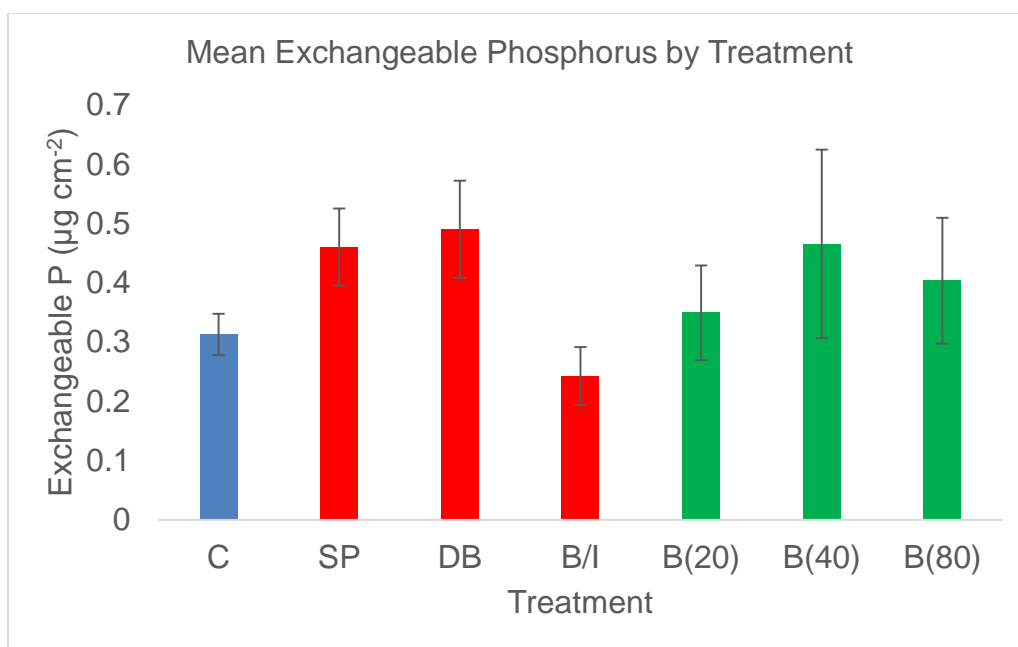


Fig. 4.19. Mean exchangeable P ($\mu\text{g P cm}^{-2}$) as a function of fertilizer P application method measured at the soil-runoff water interface during a simulated runoff experiment. Error bars represent the standard error of the four replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); DB: Deep band ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B/I: Broadcast with incorporation ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(20): Broadcast ($20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); B(40): Broadcast ($40 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$); and B(80): Broadcast ($80 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

4.5.2.3 Total phosphorus content in the particulate fraction

Following the simulated run-off experiment, an acid digest (Tiessen and Moir, 2008) was conducted to determine total P concentration of the particulate fraction collected on the membrane filter after run-off samples were filtered through a $0.45 \mu\text{m}$ membrane filter. The results of this procedure are presented in Fig. 4.20. No statistically significant treatment effect on total P concentration in the particulate P fraction was observed ($P=0.66$).

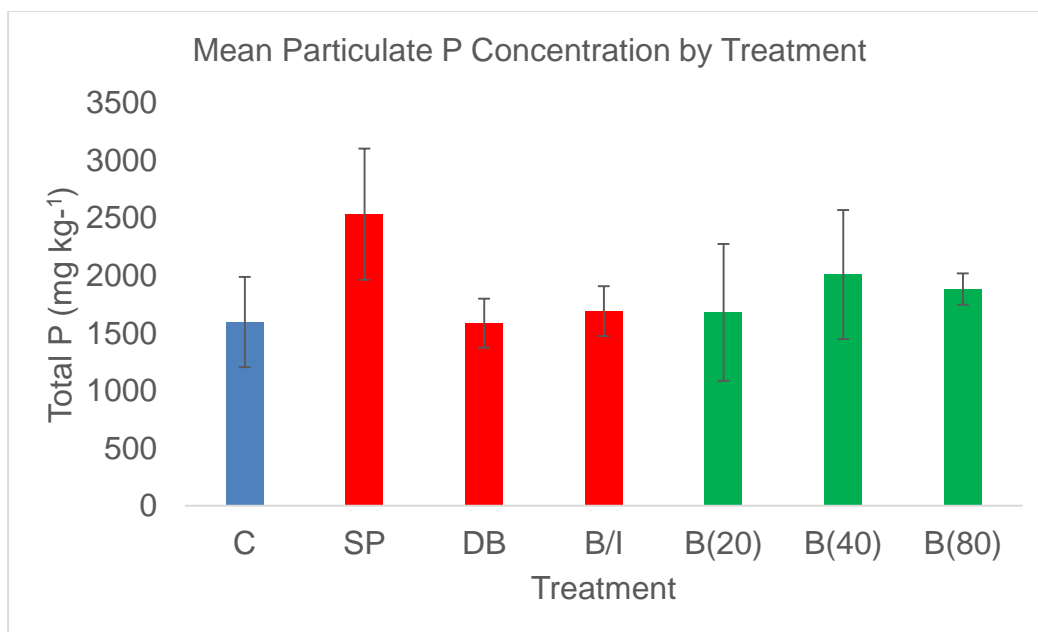


Fig. 4.20. Mean total P concentration (mg kg⁻¹) of the particulate fraction collected following vacuum filtration of runoff water samples from a simulated runoff experiment as a function of fertilizer P application method. Error bars represent the standard error of the four replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

4.5.3 Freeze-thaw cycle experiment

4.5.3.1 Phosphorus release from soybean residue

The P release from soybean residue following a simulated freeze-thaw cycle was not significantly influenced by fertilizer P application method ($P=0.66$) on samples collected from the Downslope site. When considering P release following the freeze-thaw event from soybean residue sampled from the Upslope site, even greater variability was observed among treatments and there was no significant effect of fertilizer P application method ($P=0.84$; Fig. 4.22). There was a trend for soybean residue from P fertilized treatments to have greater P release compared to the unfertilized control. Significant correlations were observed between the amount of soybean residue added during the freeze-thaw cycle experiment and the amount of P released to the water at both the Downslope and Upslope locations ($P<0.001$; $r=0.60$ and $P=0.03$; $r=0.39$, respectively). Additionally, a strong correlation was observed between soybean straw P uptake

and the P release after a simulated freeze-thaw cycle at both the Downslope and Upslope positions ($P<0.001$; $r=0.73$ and $P<0.001$; $r=0.78$, respectively).

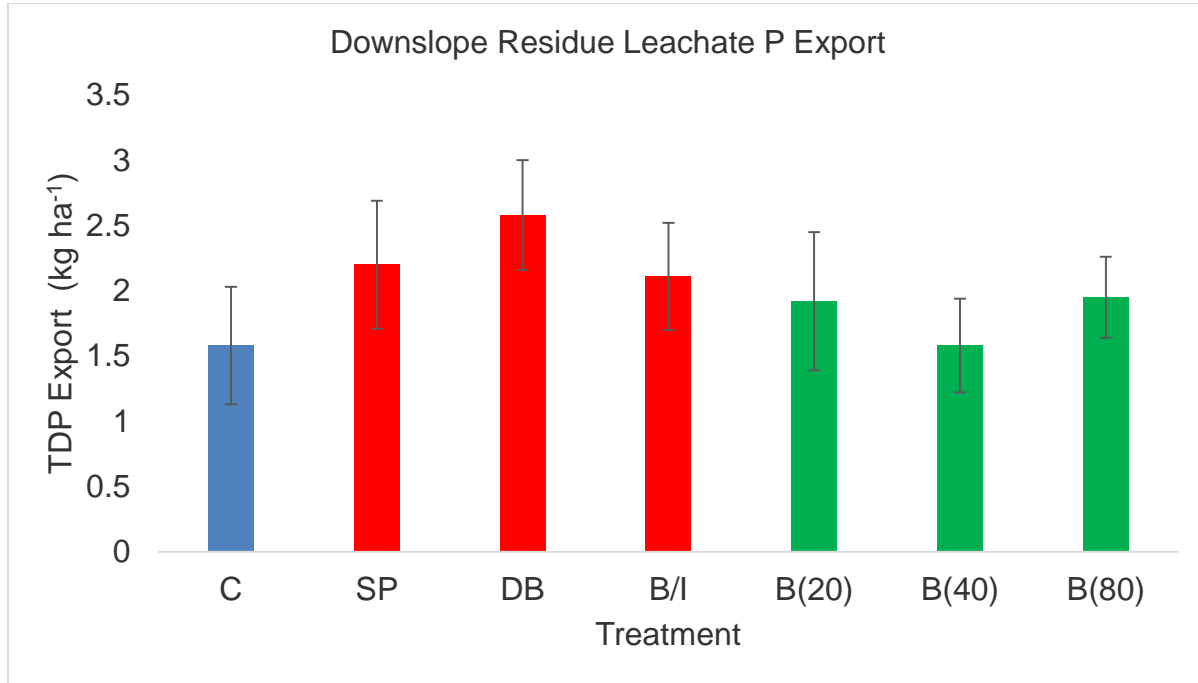


Fig. 4.21. TDP (Total Dissolved Phosphorus) export (kg TDP ha⁻¹) from water leaching soybean residue after a simulated freeze-thaw cycle at the Downslope position. Error bars represent the standard error of the four field replicates of each treatment. A description the of the treatments is as follows: C: Control; (no P) SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

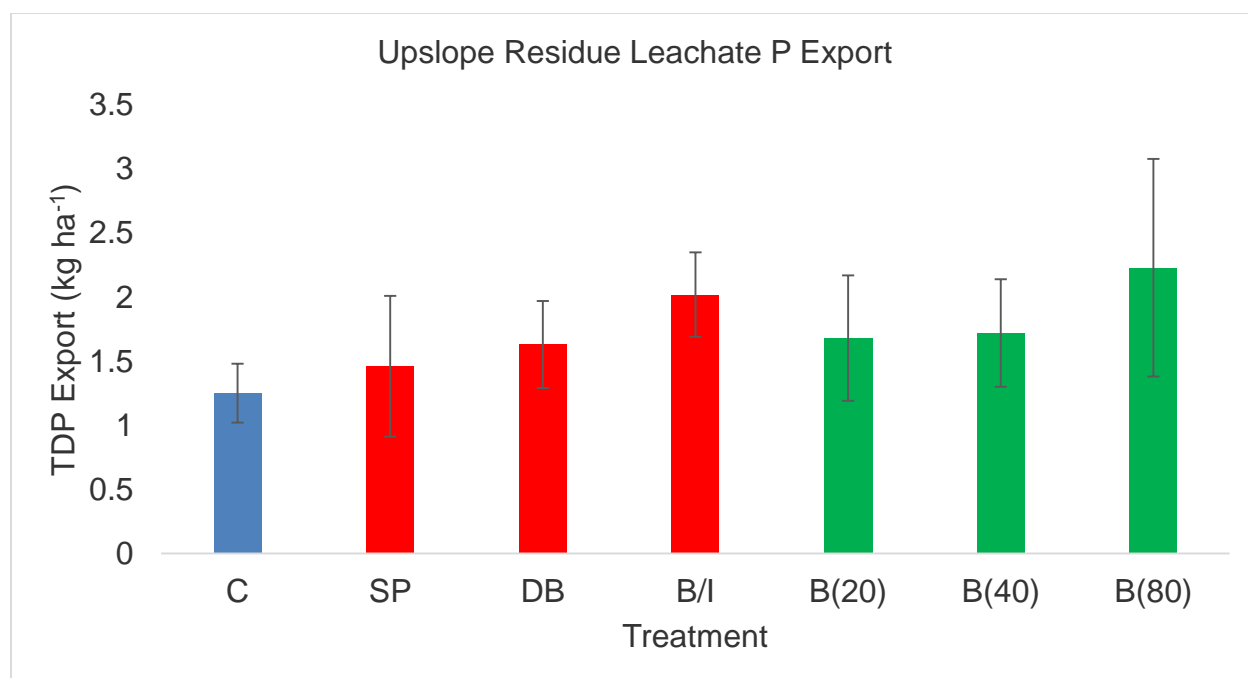


Fig. 4.22. TDP (Total Dissolved Phosphorus) export (kg TDP ha⁻¹) from soybean residue after a simulated freeze-thaw cycle at the Upslope position. Error bars represent the standard error of the four field replicates of each treatment. A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹). Red coloured bars collectively denote in-soil placement of P fertilizer while green coloured bars indicate surface broadcast placement. Blue is the unfertilized control.

4.5.3.2 Total P content of leached soybean residue

An acid digest of the soybean residue was conducted before and after the freeze-thaw leaching to measure total P (Table 4.1) and a mass balance approach was used to calculate P loss from soybean residue during the simulated cycle. Fertilizer P application method did not significantly affect total P concentration of soybean residue following the freeze-thaw cycle, nor P loss during the experiment ($P > 0.10$).

Table 4.1 Mean total P concentration of soybean residue before and after a simulated freeze-thaw leaching for the Downslope and Upslope positions. Means (n=4) within a row followed by different letters are significantly different (Tukey's $P < 0.05$).

	Treatment [†]							<i>P</i> Value
	C	SP	DB	B/I	B(20)	B(40)	B(80)	
	-----mg kg ⁻¹ -----							
	Downslope							
Residue P	696.4 ^{ab}	750.9 ^{ab}	683.5 ^b	815.6 ^{ab}	731.4 ^{ab}	1058.1 ^a	967.4 ^{ab}	0.0262
Leached Residue P	170.3 ^a	161.0 ^a	197.6 ^a	236.2 ^a	225.9 ^a	207.2 ^a	226.6 ^a	0.1336
P Loss	513.1 ^a	590.0 ^a	485.9 ^a	579.4 ^a	532.3 ^a	767.7 ^a	680.2 ^a	0.2060
	Upslope							
Residue P	784.2 ^a	692.8 ^a	860.1 ^a	933.7 ^a	933.5 ^a	742.0 ^a	898.0 ^a	0.9037
Leached Residue P	253.1 ^a	205.0 ^a	290.6 ^a	166.9 ^a	176.6 ^a	213.2 ^a	213.8 ^a	0.3736
P Loss	569.1 ^a	557.2 ^a	605.2 ^a	766.8 ^a	756.9 ^a	456.6 ^a	684.2 ^a	0.7690

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

4.6 DISCUSSION

4.6.1 Soil phosphorus characterization

4.6.1.1 Residual soil phosphorus distribution

The results of the study show that, at least from a qualitative standpoint, fertilizer application method influences P distribution in the soil profile after a season of crop growth. Particularly, enrichment in plant available P concentrations measured at the place of fertilizer application was consistently observed for all treatments except when fertilizer P was broadcast at a rate of 80 kg P₂O₅ ha⁻¹ without incorporation. This observed inconsistency may be a reflection of the large degree of microscale variability in measured nutrient concentrations when fertilizer is applied when little soil disturbance occurs such as under the conservation tillage management system commonly practiced on the Canadian prairies. For example, Hu et al. (2014) suggested that the extraction of a strip 35 cm in length is required during soil sampling to obtain a representative sample of extractable P in no-till fields. As plant available P concentrations were measured on soil samples collected after a year of crop growth, the influence of placement on residual soil P is still evident at the point of fertilizer application, even with significant soil P depletion by soybean growth and P uptake. This agrees with Borges and Mallarino (2000), who observed a 207% enrichment in STP in the surface (0 to 7 cm) layer of soil relative to the 7.5 to 15 cm soil layer measured at the conclusion of a five year soybean-corn rotation that had received broadcast fertilizer P annually. As deep banded fertilizer P application directly below the seed resulted in STP enrichment at a greater depth in the soil profile compared to other application strategies, this application strategy may be an effective management practice to consider to prevent the off-site transport of P in run-off water (Randall and Vetsch, 2008). The significant soil P enrichment near the soil surface resulting from broadcast fertilizer application (Fig. 4.7, Fig. 4.11, and Fig. 4.12) as observed in the current study and previous studies is anticipated to promote off-site transport of P in run-off water (McIsaac et al., 1995). This was

demonstrated in the results of the simulated snowmelt run-off study discussed later in this section.

4.6.1.2 Soil phosphorus speciation

Phosphorus XANES spectroscopy

The XANES spectroscopy revealed that, qualitatively, speciation of soil fertilizer P reaction products is influenced by fertilizer application strategy. Unique features in the spectra collected from standard phosphate compounds can be used to identify the speciation of an unknown sample. For example, spectra collected from Ca-PO₄ standards show a characteristic post-edge shoulder between 2156 and 2166 eV, with the feature increasing in prominence as Ca concentration increases (Hesterberg et al., 1999). Kar et al. (2012) showed that the spectra collected from the Fe-PO₄ mineral strengite displayed a unique pre-edge feature at approximately 2148 eV which increases with crystallinity. This same characteristic pre-edge features was also observed when P was adsorbed on an Fe oxide. Qualitatively, the XANES spectra from soils in this thesis research provide indications of Fe-PO₄ minerals or P adsorbed to Fe oxides existing in all soil samples, as well as Ca-PO₄ most clearly seen in the control and broadcast followed by incorporation treatments. Broadcasting and incorporation would result in the greatest degree of mixing and interaction with the calcareous Bmk horizon that underlies the thin Ap horizon in this soil.

Although no statistical analysis was attempted in this thesis work to match the spectra from known standard compounds to the spectra shown in Fig. 4.13, the work of other researchers provides support for the observation that fertilizer application method influences speciation of fertilizer reaction products in soil. In a study conducted in Kansas, USA, Khatiwada et al. (2012) employed PCA and LCF with spectra collected from standard compounds and observed that broadcast MAP resulted in soil P existing predominantly as Ca-PO₄ minerals (66.2%), with a lesser proportion existing as adsorbed-P forms (28.7%). On the other hand, MAP applied in a band caused a much greater fraction of the soil P to exist as adsorbed-P (53.9 %), with 38.5% found as Ca-PO₄ minerals (Khatiwada et al., 2012).

Information regarding the relative concentration of P in soil samples may be inferred by examining the relative peak heights of spectra in Fig. 4.13. For example, accounting for the fact

that spectra were stacked, the measured peak intensity for the deep band treatment is noticeably higher than all other spectra. Extractable P values measured from these same soils revealed that the highest concentration of PO_4^- -P was also measured at the point of application when fertilizer P was applied in a deep band. In a field scale study where fertilizer P was band applied, the peak intensity of measured spectra was significantly higher for samples collected in the band compared to those collected at a 5 cm horizontal distance from the band centre. Wet chemical analyses of samples collected from these two positions confirmed that STP values were higher at the band centre compared to those collected away from the band (Kar et al., 2012).

4.6.1.3 Sequential chemical extraction

Fertilizer P application method influenced soil P distribution in the various pools measured through a sequential chemical extraction. The solution used in each extraction procedure attempts to separate P pools according to their lability, and potential bioavailability. For example, anion resin membrane extractable P_i is considered to be freely exchangeable, while 0.5M NaHCO_3 extracts an P_i pool that is considered to be plant available (Tiessen and Moir, 2008). Therefore, the greater P concentrations in these pools for the broadcast and incorporation treatment relative to the control treatment suggests an increased likelihood of greater TDP in snowmelt run-off water from this treatment compared to the control. Additionally, greater P concentrations were found in more stable P_o pools, such as 0.1 M NaOH and 1.0M HCl for the broadcast and incorporation treatment relative to the control and when fertilizer P was applied in a band below the seed row. Greater extractable P concentrations in these pools suggests that this treatment may have promoted microbial activity, decomposition, and immobilization of fertilizer P by microorganisms. Previous research has shown that microbial immobilization may result in the transformation of P_i to P_o in the soil solution and that both mineralization and immobilization may occur in soil simultaneously and continuously (Flaten et al., 2003). Douglas and Albrecht (2000) demonstrated that a C:P ratio of straw greater than 300:1 promotes P immobilization. Due to the low P fertility of the soil in this study, it is anticipated that the wheat stubble on which soybeans were grown would be of low P concentration, although it was not measured. Further, Sharpley et al. (1991) determined that 0.1M NaOH was an effective solution to extract biologically active P in agricultural run-off. This, in combination with the observed tendency for P concentrations in the various extracted pools for the deep band and control treatment to be

quite similar, suggests that application of fertilizer P in a band below the seed row may be considered an effective strategy to mitigate the off-site transport of applied P by causing the applied P to remain in less mobile forms.

4.6.2 Simulated run-off experiment

4.6.2.1 Total dissolved phosphorus export

Total dissolved phosphorus export resulting from simulated snowmelt run-off was found to be significantly influenced by fertilizer P application method ($P=0.03$). Multi-treatment comparisons revealed that mean TDP export was greatest when fertilizer P was broadcast at 20 kg P_2O_5 ha⁻¹ (0.04 kg TDP ha⁻¹), and significantly higher than the control treatment and in-soil methods (broadcast and incorporated, seed-row, and deep banded). Further, although not statistically different from the in-soil methods, broadcast application at 80 and 40 kg P_2O_5 ha⁻¹ resulted in the second and third highest mean TDP export among all treatments. These results demonstrate that broadcast fertilizer P application results in greater TDP export compared to no fertilizer application or when fertilizer P was applied in-soil. Tabarra (2003) observed that fertilizer application method (broadcast vs incorporation) had a strongly significant effect ($P<0.001$) on TDP concentration in rainfall run-off water, where incorporation of liquid fertilizer P resulted in a lower concentration of TDP (1.93 mg L⁻¹) relative to broadcast application (3.98 mg L⁻¹). The results of these studies support in soil placement of nutrient amendments as a widely accepted Best Management Practice (BMP) to limit the off-site transport of applied P in rainfall, and in spring snowmelt as demonstrated in the current study. The ability of in-soil application methods of fertilizer P to limit TDP export in run-off water is also illustrated by the fact that seed-placed, deep banded, and broadcast followed by incorporation treatments resulted in mean TDP export values in simulated snowmelt water similar to plots that had received no fertilizer P (Fig. 4.14). This agrees with the work of other researchers, who showed in a study conducted in Minnesota, USA, that TDP in rainfall runoff water from plots on which fertilizer P was broadcast and incorporated did not differ significantly from those that had not received fertilizer application (Timmons et al., 1973).

4.6.2.2 Exchangeable phosphorus at soil-run-off water interface

Fertilizer P application method did not significantly influence exchangeable P supply at the soil-runoff water interface during a simulated runoff experiment ($P=0.40$), while statistically significant differences among treatments were observed for TDP export during the run-off event. This suggests that exchangeable P supply at the surface may not be the most appropriate means to predict the off-site transport of P in snowmelt run-off water on thawing soils, because the snowmelt water on thawing soil not only interacts and moves through the surface but also through the sub-surface as it moves laterally into the collection container. Also there were no large differences among treatments in the KM extractable P in the 1 cm depth of the nailboard monolith soil samples. Sharpley et al. (2008) noted that water soluble P may be a more effective predictor of P lost during a run-off event than other chemical measures. Sharpley et al. (1991) also determined that 0.1M NaOH was an effective solution to extract biologically active P in agricultural run-off. Finally, as discussed in Chapter 3, measured nutrient concentrations from the Upslope position were highly variable, which may have prevented the observation of any treatment effect.

4.6.2.3 Total phosphorus content of particulate fraction in run-off

Previous research work has shown that land management history significantly influences the contribution that particulate phosphorus (PP) contributes to the total P load in run-off water. For example, McIsaac et al. (1995) observed that PP represents 75 to 95 % of the total P exported from land under a conventional tillage management system. Under conservation tillage, however, the total sediment load in run-off water may be drastically reduced, as particulate P becomes bound to sediment and rarely leaves the field of origin. (McIsaac et al., 1995). In a study at Swift Current, Sk, the PP was found to constitute a significantly higher proportion of P in run-off from pasture than cropland (Cade-Menun et al. 2013). The PP in run-off from pasture may be predominantly organic while that from eroding cultivated land is likely to be dominated by inorganic P minerals contained in the sediment load. Less work has been completed examining the effect that fertilizer application method has on influencing P concentration of the PP fraction, especially in Western Canada. In this study, no statistically significant differences were found among treatments for the P concentration of the PP fraction ($P=0.66$). However,

when considering the potential for water quality degradation through eutrophication, the PP fraction should not be neglected, as this fraction is a component of biologically active P which can be readily assimilated by aquatic organisms upon mineralization, desorption and/or dissolution (Ellison and Brett, 2006).

4.6.3 Freeze-thaw cycle experiment

4.6.3.1 Phosphorus release from soybean residue

The P application method was shown in this thesis work to significantly influence soybean grain P uptake and total P concentration of soybean straw. This is not surprising, as P supply measured through PRSTM anion exchange membrane resin was significantly influenced by fertilizer P application method in the Downslope position (Table 3.3) and resin P has been shown to be satisfactorily correlated to plant available P (Qian and Schoenau, 2002). As such, it was reasoned that fertilizer P application may also influence P released from soybean residue following a simulated freeze-thaw cycle. However, no significant treatment effect was observed for the amount of P released from soybean residue in the simulated freeze-thaw cycle. A field's tillage history (i.e. conventional vs conservation) has also been shown to significantly influence P release from crop residue, as significant amounts of crop residue are often left on the soil surface under a conservation tillage management system and may be a significant source of P release (Messiga et al., 2010; Liu et al., 2014).

In this study, fertilizer P application method did not have a significant effect on influencing P release from soybean residue in the presence of a simulated freeze-thaw cycle in either the Downslope or Upslope position. However, significant correlations were observed between P export and the amount of residue added for each experimental unit in the simulated freeze-thaw cycle experiment at the aforementioned locations ($P < 0.001$; $r = 0.60$ and $P = 0.03$; $r = 0.39$, respectively). It should be noted that the residue added to each experimental unit represented soybean growth over a common land area (0.0625 m^2). Therefore, although the mass of residue added to each experimental unit varied, it reflects the effect that P fertilization method has on influencing soybean yield, as described in Chapter 3. For example, the field study referenced in Chapter 3 revealed that the greatest soybean yield response occurred when fertilizer P was applied in a deep band in the Downslope position. Interestingly, although not

statistically significant, P release from soybean residue was also greatest when fertilizer P was applied in a deep band.

Although the treatment effect was not statistically significant in this study, an accounting for the contribution that residue P leachate makes to the total P released to water from an agricultural system is necessary. Sharpley (1981) noted that, during a soybean growing season, soybean biomass may contribute as much as 94.4 % of the total dissolved reactive P in run-off water. Other researchers have shown that DRP leached from alfalfa (*Medicago sativa* L.) significantly increased when the extraction took place after the crop was frozen and subsequently thawed compared to when the extraction was carried out on fresh plant material. The authors also noted that P extracted from frozen and thawed plant material increased with increasing STP, suggesting a greater risk of P loss in run-off water from plant material when grown under enriched STP conditions (Roberson et al., 2007). In the present study, in both slope positions, significant correlations between soybean straw P uptake and P release were observed, confirming our hypothesis that the amount of P released from soybean residue during a simulated freeze-thaw cycle would be a function of the P concentration of the residue.

5.0 SYNTHESIS AND CONCLUSIONS

5.1 Overview

Two studies, described in Chapter 3 of this thesis, were conducted to examine the influence of fertilizer P application method and rate on crop and residual soil test phosphorus. An understanding of the impact of P fertilizer placement on crops and soil is important, as broadcast application of fertilizer P is becoming increasingly popular among agricultural producers as a strategy to improve operational efficiency of their agricultural operations. The first study, conducted at the field scale, evaluated the effect that fertilizer P application method (seed-place, deep band below seed, broadcast and incorporate, broadcast alone) and rate had on soybean yield, P uptake and recovery, and residual soil P distribution in the soil profile after harvest. In-soil placement methods (seed-placement, deep band, broadcast and incorporation) resulted in greater yield, P uptake, and recovery than broadcast alone. Broadcasting without incorporation, especially at high rates, was shown to result in surface soil layers enriched in labile P, which leads to greater dissolved P in run-off water compared to the in-soil application strategies as revealed in Chapter 4. In-soil placement does pose challenges. For example, incorporation into the soil of broadcast P fertilizer often requires a second field operation and is not compatible with the concept of zero-till. Banding of fertilizer below or to the side of the seed row requires special equipment and many growers prefer to have some fertilizer P in the seed-row for a “starter” effect. However, there are limits to how much fertilizer P can be safely placed in the seed row with the seed, depending on the crop, row spacing, and opener spread. For soybean, these maximum safe rates had not been established for soils and equipment configurations normally used for seeding in Saskatchewan. Therefore, a second study was conducted in a controlled environment to address current recommendations for rates of fertilizer P to be applied in the seed-row for soybean grown in Saskatchewan, as described in Chapter 3. This work showed that soybean can tolerate rates of seed-placed P in a loamy textured soil of up to 20 kg P₂O₅ ha⁻¹ with a 10 to 15% seed-bed utilization, without significant reduction in germination and emergence.

To better understand the environmental implications of P fertilizer placement strategy, detailed spectroscopic and chemical evaluations of residual soil P forms were conducted and the export of P in simulated snowmelt run-off was evaluated in studies described in Chapter 4. The speciation of P in soil can influence both plant availability and the mobility of P. Previous work had shown fertilizer application method to have a significant influence on the speciation of fertilizer P reaction products in an acidic soil of the Midwest USA (Khatiwada et al., 2012). However, there were no similar studies in calcareous soils common to the Canadian prairies. Therefore, spectroscopic and chemical extraction studies were conducted, outlined in Chapter 4, with the goal to reveal the effect that fertilizer application method has on the P forms in soil after harvest. The post-harvest period was chosen because it is believed that the majority of off-site P transport in water from fields occurs in the spring snowmelt. Qualitatively, P concentrations in various soil P pools were influenced by fertilizer P application method. Generally, broadcast fertilizer P application, with and without incorporation, resulted in the higher concentrations of labile, and thus potentially mobile, organic P forms and water soluble P in the surface soil layer than the control or deep banded treatments. Broadcasting may enhance microbial immobilization of fertilizer P into microbial biomass due to greater interaction with crop residues. Fertilizer application method was found to have a significant influence on P export in simulated snowmelt run-off water. In general, broadcast fertilizer P application resulted in greater P export in run-off water compared to in-soil placement methods. Additionally, seed-placed and banded application of fertilizer P below the seed row resulted in measured P export values similar to the unfertilized control treatment.

5.2 Synthesis and Recommendations

Four R Nutrient Stewardship has been proposed as an effective framework for the creation and implementation of agricultural best management practices (BMP's) related to the application of fertilizer. As a part of this framework, an agricultural producer should consider the right source, right rate, right time, and right place when making decisions about fertilizer application. The work in this thesis supports the implementation of several agricultural BMP's that fit within the Four R Nutrient Stewardship framework, specifically regarding the right place and the right rate of fertilizer application.

The findings of this thesis work suggest that in-soil placement of fertilizer P, especially in a band, may be considered an effective BMP to achieve the greatest soybean yield response, as well as limit the potential off-site transport of applied P. At the Downslope position site, the two highest rates of broadcast application resulted in water soluble P concentrations in the surface soil layer greater than 9.7 mg P kg^{-1} , which has been suggested as a critical concentration above which adverse effects on surface water quality may be anticipated (Messiga et al., 2010). At the Upslope position site, broadcast application of fertilizer P at $20 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ resulted in mean P export of $0.04 \text{ kg TDP ha}^{-1}$, while placement in a deep band resulted mean P export of $0.009 \text{ kg TDP ha}^{-1}$, which was similar to P export with no fertilizer P application. When considering export of applied P on a watershed scale, as in the case of Lake Winnipeg with a watershed of 95.3 million ha, the difference in TDP export between the two above fertilizer application methods is substantially amplified. A consideration of fertilizer application rate, in conjunction with application method, also supports in soil placement of fertilizer P as a BMP. In this thesis, broadcast application of fertilizer P was not able to achieve the same soybean grain yield response or fertilizer P recovery as any of the three in-soil application strategies, even at a four-fold rate of application. Given that fertilizer is often the largest input cost for growers, this observation is of particular interest to agricultural producers as they strive to maintain a financially sustainable agricultural operation. In this way, in-soil placement of fertilizer P as a BMP is both environmentally and agronomically advantageous, and is consistent with the objectives of 4R Nutrient Stewardship.

Recent work has also shown that the inclusion of certain crops into rotations on the Canadian prairies that are sensitive to high rates of seed-placed fertilizer P may lead to depletion of STP over time, as more soil P is removed from the field in the form of crop grain than can be safely applied (Grant, 2012). The controlled environment experiment conducted in this thesis has shown that the safe rate of fertilizer P application in the seed-row for soybean may be 20 or 30 $\text{kg P}_2\text{O}_5 \text{ ha}^{-1}$ without causing a statistically significant reduction in soybean seedling emergence or early season biomass production. This agricultural BMP may prove beneficial in helping to mitigate potential STP depletion from occurring and further highlights the importance of a consideration of the right rate when making fertilizer application decisions.

5.3 Future Research

Several important research questions arise from this thesis work which, if investigated, may help improve the general understanding of effective fertilizer P management practice on the Canadian prairies. For example, it may be beneficial to evaluate the speciation of P_o forms in the particulate P fraction in run-off water through the use of ^{31}P NMR spectroscopy. Relationships between P_o speciation in the particulate P fraction of run-off water and operationally defined P_o pools in run-off water measured through traditional wet chemical techniques may lead to better predictions of P export in snowmelt run-off water. An improved understanding of the fate of P_o forms in snowmelt run-off water may prove beneficial, as previous work has shown that P_o forms represent a substantial proportion of the total P pool in Saskatchewan soils (Tiessen et al., 1982).

Unfortunately in this study, due to the sampling strategy employed and the inherent variability of soil properties measured at the Upslope position site, direct relationships between extractable P concentrations and P export in run-off water were not observed. For this reason, a simulated run-off experiment conducted on soil slabs removed from a study site more uniform in inherent soil properties would be useful. In this way, direct relationships between water soluble P concentrations in surface soil layers and P export in snowmelt run-off water, may be established for a number of different soil types.

Finally, it should be noted that the current study was only conducted over one season of crop growth. It may be beneficial, therefore, to assess the effect that successive applications of fertilizer P by the various application methods has on influencing residual soil P distribution and the off-site transport of applied P in snowmelt run-off water. Additionally, the aforementioned variables were only assessed following the growth of one crop, namely soybean. As different crops exhibit particular demands for soil P, and possess unique patterns of growth and root morphology, it may be beneficial to assess long-term soil P dynamics over time for a suite of crops in rotation. Future research may show that particular BMP's may be recommended for each crop in rotation to improve sustainability of agricultural operations.

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APPENDIX

A.1 Additional Statistical Information

Table A1 Selected physical and chemical soil characteristics for the Downslope position sampled in fall 2014. Values are means of soil cores collected from the four replicates of each treatment. Values within a row followed by a different letter are significantly different ($P < 0.10$). Tukey's Honestly Significant Difference ($P < 0.05$) method was used for multi-treatment comparisons.

		Treatment [†]							
	Depth (cm)	C	SP	DB	B/I	B(20)	B(40)	B(80)	<i>P</i> Value
		-----mg kg ⁻¹ -----							
NO ₃ ⁻	0-5	5.5 ^{abc}	7.3 ^{ab}	4.9 ^{bc}	8.0 ^a	5.5 ^{abc}	3.4 ^c	4.2 ^c	0.0007
	5-10	2.9 ^a	2.5 ^a	2.4 ^a	4.0 ^a	2.5 ^a	1.5 ^a	1.4 ^a	0.0760
	10-30	1.0 ^a	0.9 ^a	1.0 ^a	1.0 ^a	1.0 ^a	0.7 ^a	0.7 ^a	0.1715
K ⁺	0-5	566.0 ^a	567.1 ^a	535.4 ^a	594.1 ^a	499.1 ^a	536.0 ^a	504.4 ^a	0.2895
	5-10	399.0 ^a	358.6 ^a	348.3 ^a	389.1 ^a	343.5 ^a	332.2 ^a	298.6 ^a	0.1991
	10-30	232.8 ^a	226.5 ^a	231.5 ^a	242.4 ^a	228.4 ^a	127.1 ^b	105.2 ^b	<0.0001
SO ₄ ²⁻	0-5	4.2 ^{ab}	5.7 ^a	4.7 ^{ab}	4.2 ^{ab}	4.0 ^{ab}	2.5 ^b	3.4 ^{ab}	0.0597
	5-10	3.5 ^a	3.5 ^a	3.1 ^a	3.3 ^a	2.4 ^a	2.1 ^a	3.4 ^a	0.8378
	10-30	2.4 ^a	7.4 ^a	6.0 ^a	3.5 ^a	6.0 ^a	3.1 ^a	8.0 ^a	0.7380
pH	0-5	7.3 ^a	7.4 ^a	7.4 ^a	7.2 ^a	7.1 ^a	7.3 ^a	7.3 ^a	0.8893
	5-10	7.0 ^a	7.0 ^a	7.0 ^a	7.0 ^a	7.2 ^a	7.2 ^a	7.3 ^a	0.7085
	10-30	7.5 ^a	7.5 ^a	7.5 ^a	7.4 ^a	7.7 ^a	8.0 ^a	8.0 ^a	0.1680
		-----dS m ⁻¹ -----							
EC [‡]	0-5	0.3 ^a	0.4 ^a	0.3 ^a	0.3 ^a	0.1 ^a	0.2 ^a	0.3 ^a	0.3405
	5-10	0.1 ^a	0.1 ^a	0.1 ^a	0.1 ^a	0.1 ^a	0.2 ^a	0.1 ^a	0.2859
	10-30	0.3 ^a	0.3 ^a	0.3 ^a	0.3 ^a	0.3 ^a	0.5 ^a	0.4 ^a	0.6162
		-----%-----							
OC [§]	0-5	2.0 ^a	2.1 ^a	2.0 ^a	2.1 ^a	2.0 ^a	1.9 ^a	1.9 ^a	0.1502

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

[‡]EC= Electrical Conductivity

[§]OC= Organic Carbon

Table A2 Selected physical and chemical soil characteristics for the Upslope position in fall 2014. Values are means of soil cores collected from the four replicates of each treatment. Values within a row followed by a different letter are significantly different ($P<0.10$). Tukey's Honestly Significant Difference ($P<0.05$) method was used for multi-treatment comparisons.

	Depth (cm)	C	SP	DB	Treatment [†]				<i>P</i> Value
					B/I	B(20)	B(40)	B(80)	
					-----mg kg ⁻¹ -----				
NO ₃ ⁻	0-5	2.5 ^a	3.1 ^a	2.6 ^a	3.3 ^a	2.4 ^a	2.5 ^a	3.1 ^a	0.9016
	5-10	1.2 ^a	1.1 ^a	1.1 ^a	1.9 ^a	1.1 ^a	1.3 ^a	1.3 ^a	0.3170
	10-30	0.7 ^a	0.7 ^a	0.6 ^a	0.9 ^a	0.6 ^a	0.7 ^a	0.9 ^a	0.1595
K ⁺	0-5	380.8 ^a	389.8 ^a	372.7 ^a	435.5 ^a	421.4 ^a	308.2 ^a	328.1 ^a	0.0817
	5-10	259.0 ^a	224.2 ^a	213.3 ^a	261.2 ^a	251.2 ^a	161.7 ^a	161.1 ^a	0.1249
	10-30	198.7 ^a	155.8 ^a	154.5 ^a	207.0 ^a	177.6 ^a	113.2 ^a	192.6 ^a	0.6239
SO ₄ ²⁻	0-5	2.2 ^a	2.2 ^a	2.8 ^a	2.2 ^a	2.4 ^a	2.0 ^a	2.8 ^a	0.9790
	5-10	1.4 ^a	1.8 ^a	2.2 ^a	1.4 ^a	2.1 ^a	1.1 ^a	4.1 ^a	0.1875
	10-30	1.6 ^a	2.3 ^a	3.8 ^a	0.9 ^a	3.3 ^a	1.8 ^a	1.1 ^a	0.0958
pH	0-5	7.5 ^a	7.5 ^a	7.4 ^a	7.6 ^a	7.7 ^a	7.6 ^a	7.5 ^a	0.1381
	5-10	7.6 ^a	7.5 ^a	7.6 ^a	7.6 ^a	7.7 ^a	7.5 ^a	7.2 ^a	0.0769
	10-30	8.0 ^a	7.9 ^a	7.8 ^a	7.8 ^{ab}	7.9 ^{ab}	7.7 ^{ab}	7.5 ^b	0.0119
EC [‡]					-----dS m ⁻¹ -----				
	0-5	0.3 ^a	0.3 ^a	0.1 ^a	0.3 ^a	0.4 ^a	0.4 ^a	0.3 ^a	0.1159
	5-10	0.3 ^a	0.2 ^a	0.2 ^a	0.3 ^a	0.3 ^a	0.2 ^a	0.3 ^a	0.7774
	10-30	0.4 ^a	0.4 ^{ab}	0.3 ^{ab}	0.3 ^{ab}	0.3 ^{ab}	0.2 ^b	0.3 ^{ab}	0.0769
OC [§]					-----%-----				
	0-5	1.5 ^a	1.5 ^a	1.5 ^a	1.6 ^a	1.5 ^a	1.7 ^a	1.7 ^a	0.0543

[†]A description the of the treatments is as follows: C: Control (no P); SP: Seed-placed (20 kg P₂O₅ ha⁻¹); DB: Deep band (20 kg P₂O₅ ha⁻¹); B/I: Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); B(20): Broadcast (20 kg P₂O₅ ha⁻¹); B(40): Broadcast (40 kg P₂O₅ ha⁻¹); and B(80): Broadcast (80 kg P₂O₅ ha⁻¹).

[‡]EC= Electrical Conductivity

[§]OC= Organic Carbon

Table A3 Mean grain, straw, and total N uptake and N recovery measured in fall 2014 from the Downslope and Upslope positions. Means with different letters are significantly different (Tukey's HSD, $P < 0.05$).

Parameter	Treatment [†]							<i>P</i> Value
	C	SP	DB	B/I	B(20)	B(40)	B(80)	
	Downslope							
Grain N Uptake (kg ha ⁻¹)	118.6 ^a	160.2 ^a	179.1 ^a	115.8 ^a	123.1 ^a	105.7 ^a	121.2 ^a	0.07
Straw N Uptake (kg ha ⁻¹)	57.5 ^a	49.7 ^a	46.7 ^a	43.3 ^a	49.9 ^a	53.4 ^a	54.0 ^a	0.90
Total N Uptake (kg ha ⁻¹)	176.1 ^a	209.9 ^a	225.9 ^a	157.5 ^a	173.0 ^a	159.1 ^a	175.2 ^a	0.28
	Upslope							
Grain N Uptake (kg ha ⁻¹)	121.7 ^a	115.4 ^a	110.2 ^a	157.2 ^a	101.5 ^a	145.8 ^a	151.6 ^a	0.65
Straw N Uptake (kg ha ⁻¹)	46.7 ^a	37.2 ^a	56.4 ^a	59.0 ^a	41.2 ^a	43.6 ^a	48.4 ^a	0.61
Total N Uptake (kg ha ⁻¹)	168.5 ^a	152.7 ^a	166.6 ^a	229.1 ^a	161.6 ^a	189.3 ^a	200.0 ^a	0.61

[†] A description the of the treatments is as follows: 1) Control; 2) Seed-placed (20 kg P₂O₅ ha⁻¹); 3) Deep band (20 kg P₂O₅ ha⁻¹); 4) Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); 5) Broadcast (20 kg P₂O₅ ha⁻¹); 6) Broadcast (40 kg P₂O₅ ha⁻¹); and 7) Broadcast (80 kg P₂O₅ ha⁻¹).

Table A4 Soil P pools from sequential chemical extraction procedure as a function of fertilizer application method and sampling position.

Trt [†]	Position	Resin	Fraction								
			NaHCO ₃ P _t	NaHCO ₃ P _i	NaHCO ₃ P _o	NaOH P _t	NaOH P _i	NaOH P _o	HCl P _t	HCl P _i	HCl P _o
			µg P g ⁻¹								
C	Seed Row	10.1	17.8	4.8	13.0	65.7	18.7	47.0	300.4	141.5	158.9
C	10 cm Horizontal	22.3	49.0	15.4	33.6	77.7	28.8	48.8	323.0	160.8	162.2
SP	Seed Row	22.8	38.2	23.5	14.6	79.9	29.4	50.6	290.6	139.3	151.3
SP	10 cm Horizontal	11.6	17.5	4.1	13.4	66.7	18.8	47.9	286.6	135.7	150.9
DB	Seed Row	10.7	23.5	10.0	13.6	68.7	21.5	47.2	303.3	149.5	153.8
DB	10 cm Horizontal	19.6	58.1	7.6	50.4	77.7	24.1	53.6	301.7	147.8	153.9
B/I	Seed Row	15.0	31.2	5.6	25.6	79.4	20.9	58.5	338.9	157.9	181.0
B/I	10 cm Horizontal	16.6	21.1	11.5	9.6	85.4	27.9	57.4	396.0	191.0	205.0
B/I	10 cm Horizontal	15.0	15.8	2.1	13.8	66.2	16.7	49.6	325.4	154.4	170.9
	at 7 cm Depth										
B(20)	Seed Row	11.1	25.7	29.1	0	77.2	23.8	53.3	362.0	163.3	198.7
B(20)	10 cm Horizontal	11.2	18.0	2.2	15.8	67.2	16.7	50.6	314.5	150.4	164.1
B(40)	Seed Row	22.9	17.3	4.4	12.9	66.2	21.8	44.4	333.3	156.1	177.2
B(40)	5 cm Horizontal	67.7	80.6	71.4	9.2	128.5	69.4	59.1	373.4	185.9	187.6
B(40)	10 cm Horizontal	31.0	21.1	9.3	11.8	65.0	24.9	40.1	347.7	165.6	182.1
B(80)	Seed Row	19.1	15.4	3.5	11.9	63.2	21.5	41.7	309.7	148.2	161.5
B(80)	10 cm Horizontal	28.9	16.1	2.2	13.9	59.5	17.8	41.7	342.1	168.1	174.0

[†]Trt= Treatment; A description the of the treatments is as follows: 1) Control; 2) Seed-placed (20 kg P₂O₅ ha⁻¹); 3) Deep band (20 kg P₂O₅ ha⁻¹); 4) Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); 5) Broadcast (20 kg P₂O₅ ha⁻¹); 6) Broadcast (40 kg P₂O₅ ha⁻¹); and 7) Broadcast (80 kg P₂O₅ ha⁻¹).

Table A5 Mean grain, straw, and total P and N concentration measured in Fall 2014 from the Downslope and Upslope positions. Means with different letters are significantly different (Tukey's HSD, $P < 0.05$).

Parameter ($\mu\text{ g}^{-1}$)	Treatment [†]							<i>P</i> Value
	1	2	3	4 Downslope	5	6	7	
Grain P Concentration	4686.3 ^a	5019.5 ^a	4704.7 ^a	4929.4 ^a	4717.3 ^a	4813.6 ^a	5075.4 ^a	0.89
Straw P Concentration	971.9 ^a	750.9 ^a	683.5 ^a	815.6 ^a	734.5 ^a	1058.1 ^a	967.4 ^a	0.14
Total P Concentration	5555.9 ^a	5770.5 ^a	5388.3 ^a	5813.2 ^a	5659.8 ^a	5871.8 ^a	6042.8 ^a	0.91
Grain N Concentration	48298.3 ^a	48910.8 ^a	47727.2 ^a	46795.1 ^a	48082.6 ^a	46075.8 ^a	47136.9 ^a	0.16
Straw N Concentration	11143.0 ^a	8808.0 ^a	7638.6 ^a	9429.6 ^a	10906.6 ^a	12465.3 ^a	11948.6 ^a	0.17
Total N Concentration	59441.2 ^a	57718.9 ^a	55365.8 ^a	57451.4 ^a	58989.2 ^a	58541.1 ^a	59085.6 ^a	0.39
	Upslope							
Grain P Concentration	4245.9 ^a	4540.6 ^a	4470.1 ^a	4461.0 ^a	4050.4 ^a	4489.6 ^a	4755.2 ^a	0.56
Straw P Concentration	784.2 ^a	692.8 ^a	860.1 ^a	933.7 ^a	933.4 ^a	742.0 ^a	897.9 ^a	0.90
Total P Concentration	5030.1 ^a	5233.4 ^a	5330.3 ^a	5394.6 ^a	4983.9 ^a	5231.5 ^a	5653.1 ^a	0.88
Grain N Concentration	46633.7 ^a	47450.8 ^a	47821.4 ^a	46809.9 ^a	46462.6 ^a	47467.0 ^a	47791.0 ^a	0.76
Straw N Concentration	11096.7 ^a	9260.5 ^a	13136.8 ^a	9732.0 ^a	10244.5 ^a	10085.3 ^a	10840.8 ^a	0.79
Total N Concentration	59600.9 ^a	53470.4 ^a	60958.2 ^a	59882.4 ^a	60195.7 ^a	57552.3 ^a	57735.9 ^a	0.35

[†] A description the of the treatments is as follows: 1) Control; 2) Seed-placed (20 kg P₂O₅ ha⁻¹); 3) Deep band (20 kg P₂O₅ ha⁻¹); 4) Broadcast with incorporation (20 kg P₂O₅ ha⁻¹); 5) Broadcast (20 kg P₂O₅ ha⁻¹); 6) Broadcast (40 kg P₂O₅ ha⁻¹); and 7) Broadcast (80 kg P₂O₅ ha⁻¹)

Table A6 Analysis of variance examining the relationship between the fixed effect of fertilizer P application method (control, seed-placed, deep band, broadcast with incorporation, broadcast at 20 kg P₂O₅ ha⁻¹, broadcast at 40 kg P₂O₅ ha⁻¹, and broadcast at 80 kg P₂O₅ ha⁻¹) on MK extractable P (mg kg⁻¹), H₂O Sol P (mg kg⁻¹), and Resin P (µg cm⁻²) from soil cores collected from two sites within a field located near Central Butte Saskatchewan in Fall 2014 (corresponds to Tables 3.3 and 3.4).

Site	Dependent Variable	Fixed Effect	Num df [†]	F-value	<i>P</i> Value	SEM [‡]	
Downslope	MK P [§] (mg kg ⁻¹)	0-5 cm	Fertilizer	6	6.54	0.0009	2.69
		5-10 cm	application	6	2.32	0.0951	0.50
		10-30 cm	method	6	4.99	0.0046	0.13
	H ₂ O Sol P [¶] (mg kg ⁻¹)	0-5 cm	Fertilizer	6	6.35	0.0010	1.23
		5-10 cm	application	6	1.25	0.3317	0.32
		10-30 cm	method	6	1.17	0.3673	0.21
	Resin P (μg cm ⁻²)	0-5 cm	Fertilizer	6	10.56	<0.0001	0.19
		5-10 cm	application	6	1.71	0.1792	0.04
		10-30 cm	method	6	4.52	0.0073	0.01
Upslope	MK P [§] (mg kg ⁻¹)	0-5 cm	Fertilizer	6	1.33	0.2951	4.40
		5-10 cm	application	6	3.30	0.0273	0.52
		10-30 cm	method	6	1.17	0.3667	0.18
	H ₂ O Sol P [¶] (mg kg ⁻¹)	0-5 cm	Fertilizer	6	1.28	0.3072	1.85
		5-10 cm	application	6	1.66	0.1873	0.26
		10-30 cm	method	6	0.88	0.5280	0.09
	Resin P (μg cm ⁻²)	0-5 cm	Fertilizer	6	0.82	0.5656	0.41
		5-10 cm	application	6	2.28	0.0824	0.06
		10-30 cm	method	6	3.00	0.0326	0.01

[†]Num df= numerator degrees of freedom

[‡]SEM= standard error of mean

[§]MK P= Modified Kelowna extractable phosphate, PO₄-P

[¶]H₂O Sol P= Water Soluble P

Table A7 Analysis of variance examining the relationship between the fixed effect of fertilizer P application method (control, seed-placed, deep band, broadcast with incorporation, broadcast at 20 kg P₂O₅ ha⁻¹, broadcast at 40 kg P₂O₅ ha⁻¹, and broadcast at 80 kg P₂O₅ ha⁻¹) on soybean grain and straw yield (kg ha⁻¹) and P uptake in soybean grain and straw (kg ha⁻¹) from two sites within a field near Central Butte Saskatchewan in 2014 (corresponds to Tables 3.6 and 3.7).

Site	Dependent Variable	Fixed Effect	Num df [†]	F-value	P Value	SEM [‡]
Downslope	Yield (kg ha ⁻¹)	Grain	6	2.00	0.1192	454.52
		Straw	6	1.34	0.2916	805.52
	P Uptake (kg ha ⁻¹)	Fertilizer application method				
		Grain	6	2.29	0.0834	2.06
		Straw	6	0.53	0.7759	0.79
		Fertilizer application method				
Upslope	Yield (kg ha ⁻¹)	Grain	6	0.60	0.7258	584.75
		Straw	6	0.69	0.6605	705.73
	P Uptake (kg ha ⁻¹)	Fertilizer application method				
		Grain	6	8.33	0.0002	1.33
		Straw	6	2.05	0.1195	0.62
		Fertilizer application method				

[†]Num df= numerator degrees of freedom

[‡]SEM= standard error of mean

Table A8 Analysis of variance examining the relationship between the fixed effect of fertilizer P application rate (0, 20, 40, 60, and 80 kg P₂O₅ ha⁻¹) on soybean and faba bean emergence (%) and biomass production (g) measured 14 days after seeding and grown under controlled environmental conditions (corresponds to Figures 3.6 to 3.9).

Dependent Variable	Fixed Effect	Num df [†]	F-value	P Value	SEM [‡]
Soybean Emergence (%)	Fertilizer application rate	4	17.23	<0.0001	4.43
Soybean Biomass (g)		4	7.28	0.0018	0.14
Faba Bean Emergence (%)		4	1.56	0.2364	3.29
Faba Bean Biomass (g)		4	4.60	0.0126	0.14

[†]Num df= numerator degrees of freedom

[‡]SEM= standard error of mean



ALS Laboratory Group Agricultural Services

Phone:
1-800-667-7645

SOIL TEST REPORT

Dealer / Crop Consultant:

DEPT OF SOIL SCIENCE
51 CAMPUS DRIVE
SASKATOON, SK S7N 5A8
Phone: --
Fax: --
Email: cory.fatteicher@usask.ca

Client Information:

CORY FATTEICHER

Sample / Field Information:

Crop Year 2014
Field Name BLAKE LS
Legal Location 21 4 W3
Soil Climatic Zone Brown
GPS Reference
Acres
Previous Crop
Yield
Stubble Management Spread
Rotation Continuous

Sample ID 1422396

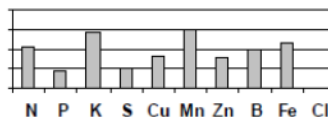
Date Sampled 08-MAY-14

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH ₄ -N (lb/ac)	Calculated CEC meq/100g	Ca	Mg	K	Na	Base Saturation Ca Mg K Na % of CEC
0-6	Clay Loam	6.6	0.1	0.2	Non Saline								

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO ₃ -N	P	K	SO ₄ -S	Cu	Mn	Zn	B	Fe	Cl	Excess Sufficient Marginal Deficient
0-6	3	18	>540	5	1.0	20.1	1.3	1.3	77		



ALS Laboratory Group

NUTRIENT RECOMMENDATION RATES (lb/ac)

		Soil Available Moisture: <input type="checkbox"/> Actual: <input checked="" type="checkbox"/> Typical: 1.5 inches									
Soybeans		N	P ₂ O ₅	K ₂ O	S	Cu	Mn	Zn	B	Fe	Cl
27 bu/ac	7.9 in. of ppt - 25% chance of this ppt.	15-25	30-35	0 or 15	10-15	0-3	0-0	4-6	0-0	0-0	
20 bu/ac	6.0 in. of ppt - 50% chance of this ppt.	10-20	25-30	0 or 15	5-10	0-3	0-0	2-4	0-0	0-0	
9 bu/ac	3.2 in. of ppt - 75% chance of this ppt.	5-15	15-20	0-0	0-10	0-3	0-0	0-2	0-0	0-0	

No Goal Submitted

☐ Irrigation

Other Recommendations And Comments

A 0 or 15 lbs/ac K₂O recommendation is made for high K soils because K may not be available to the plant in cool (particularly cool and dry) soils.

N recommendations: for legumes assume appropriate inoculation of seed. Where N fixation is compromised (cool or dry soil, inoculant application problems, etc.), starter N can improve yield, particularly when side-banded.

The P₂O₅ recommendation is based on banding or seed-placement (if rate is safe). For broadcast and incorporation the P₂O₅ rate should be 2 times that shown.

K₂O recommendation: < 30 lbs/ac are for seed-placement or banding, and > 30 lbs/ac are for broadcast and incorporation. The banding rate X 2 = the broadcast and incorporation rate.

Cu recommendations are for broadcast and incorporation of inorganic salts. One application at this rate should last several years. Consult label for application of chelates or foliar products.

Fig. A1. Soil test report from soil cores collected from the Downslope field site location in Spring 2014. A composite subsample was collected from eight individual soil cores collected in April from the marked out control plots before any treatments or field operations were conducted.



ALS Laboratory Group Agricultural Services SOIL TEST REPORT

Phone:
1-800-667-7645

Dealer / Crop Consultant:
DEPT OF SOIL SCIENCE
51 CAMPUS DRIVE
SASKATOON, SK S7N 5A8
Phone: --
Fax: --
Email: cory.fatteicher@usask.ca

Client Information:
CORY FATTEICHER

Sample / Field Information:
Crop Year 2014
Field Name BLAKE US
Legal Location 21 4 W3
Soil Climatic Zone Brown
GPS Reference
Acres
Previous Crop
Yield
Stubble Management Spread
Rotation Continuous

Sample ID 1422397

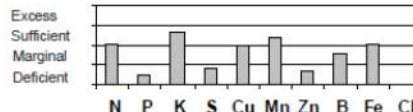
Date Sampled 08-MAY-14

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH	E.C.		Salinity Rating	Organic Matter %	NH ₄ -N (lb/ac)	Calculated CEC meq/100g	Base Saturation			
			1S:2W	1S:2W (mS/cm)					Ca	Mg	K	Na
0-6	Clay Loam	7.6	0.1	0.2	Non Saline							

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO ₃ -N		P	K	SO ₄ -S		Cu	Mn	Zn	B	Fe	Cl
	lb/ac	lb/ac			lb/ac	lb/ac						
0-6	2	10	465	4	1.3	8.7	0.6	1.0	26			



ALS Laboratory Group NUTRIENT RECOMMENDATION RATES (lb/ac)

		Soil Available Moisture: <input type="checkbox"/> Actual: <input checked="" type="checkbox"/> Typical: 1.5 inches									
Soybeans		N	P ₂ O ₅	K ₂ O	S	Cu	Mn	Zn	B	Fe	Cl
27 bu/ac	7.9 in. of ppt - 25% chance of this ppt.	15-25	40-45	0 or 15	10-15	0-0	0-0	6-8	0-0.5	0-0	
20 bu/ac	6.0 in. of ppt - 50% chance of this ppt.	10-20	35-40	0 or 15	5-10	0-0	0-0	4-6	0-0.5	0-0	
9 bu/ac	3.2 in. of ppt - 75% chance of this ppt.	5-15	20-25	0-0	0-10	0-0	0-0	2-4	0-0.5	0-0	

No Goal Submitted

☐ Irrigation

Other Recommendations And Comments

B recommendations are for annual broadcast application of an inorganic salt and based on limited research. Consult label directions for foliar application.

A 0 or 15 lbs/ac K₂O recommendation is made for high K soils because K may not be available to the plant in cool (particularly cool and dry) soils.

N recommendations for legumes assume appropriate inoculation of seed. Where N fixation is compromised (cool or dry soil, inoculant application problems, etc.), starter N can improve yield, particularly when side-banded.

The P₂O₅ recommendation is based on banding or seed-placement (if rate is safe). For broadcast and incorporation the P₂O₅ rate should be 2 times that shown.

K₂O recommendations < 30 lbs/ac are for seed-placement or banding, and > 30 lbs/ac are for broadcast and incorporation. The banding rate X 2 = the broadcast and incorporation rate.

Fig. A2. Soil test report from soil cores collected from the Upslope field site location in Spring 2014. A composite subsample was collected from eight individual soil cores collected in April from the marked out control plots before any treatments or field operations were conducted.